

122
49

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON

ORGANIC CHEMISTRY.

Committee of Publication:

H. E. ARMSTRONG, Ph.D., F.R.S.
WYNDHAM R. DUNSTAN, M.A., F.R.S.
F. S. KIPPING, D.Sc.
R. MELDOLA, F.R.S.
H. F. MORLEY, M.A., D.Sc.
HUGO MÜLLER, Ph.D., F.R.S.

W. H. PERKIN, LL.D., F.R.S.
W. J. RUSSELL, Ph.D., F.R.S.
J. MILLAR THOMSON, F.R.S.E.
T. E. THORPE, Ph.D., F.R.S.
W. P. WYNNE, D.Sc.

Editor:

C. E. GROVES, F.R.S.

Sub-Editor:

A. J. GREENAWAY.

Abstractors:

C. F. BAKER, Ph.D., B.Sc.
D. BENDIX.
A. G. BLOXAM.
C. H. BOTHAMLEY.
B. H. BROUGH.
H. G. COLMAN, Ph.D.
H. CROMPTON.
L. DE KONINGH.
W. D. HALLIBURTON, M.D., B.Sc.,
F.R.S.
A. HARDEN, M.Sc., Ph.D.
F. S. KIPPING, Ph.D., D.Sc.
A. R. LING.
D. A. LOUIS.
N. H. J. MILLER, Ph.D.

G. T. MOODY, D.Sc.
J. M. H. MUNRO, D.Sc.
T. G. NICHOLSON.
W. J. POPE.
E. W. PREVOST, Ph.D.
E. C. ROSSITER.
R. ROUTLEDGE, B.Sc.
M. J. SALTER.
W. TATE.
J. TAYLOR, B.Sc.
L. T. THORNE, Ph.D.
J. B. TINGLE, Ph.D.
J. WADE, B.Sc. (JN. W.)
J. WALKER, D.Sc., Ph.D. (J. W.)

1893. Vol. LXIV. Part I.

LONDON:

GURNEY & JACKSON, 1, PATERNOSTER ROW.

1893.

34137
20/6(94)

JOURNAL
OF
THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

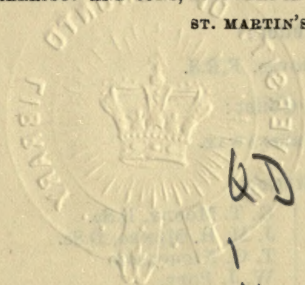
ORGANIC CHEMISTRY.

Committee of Publication:

W. H. PERKIN, F.R.S.
W. A. ROBERTS, F.R.S.
J. MILLAR THOMSON, F.R.S.
J. THOMSON, F.R.S.
W. H. WATKINS, F.R.S.

LONDON:

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY,
ST. MARTIN'S LANE.



6D

1

C6

V. 64

cop3

1888, Vol. LXIV, Part I.

GURNEY & JACKSON, 1, PATERNOSTER ROW.

1888.

CONTENTS.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS —

PART I.

Organic Chemistry.

	PAGE
HINRICHS (G.). Mechanical Comparison between the Cyanogen Radicle and the Halogens	i, 1
WALFISZ (B.). Action of Hydriodic Acid on Carbon Tetrachloride.	i, 1
LESPIEAU. Action of Zinc on Bromo-derivatives of Tricarbon Nuclei	i, 1
PERATONER (A.). Action of Iodine on Derivatives of Acetylene	i, 2
BIGOT (A.). Some Derivatives of Glycerol	i, 3
LOEW (O.). Characterisation of Sugars	i, 4
LINTNER (C. J.). Formation of Dextrose from Starch	i, 4
LINTNER (C. J.) and G. DÜLL. Preparation of Isomaltose	i, 5
MÜHLHAÜSER (O.). Higher Nitro-derivatives of Starch	i, 6
LINEBARGER (C. E.). Molecular Masses of Dextrin and Gum Arabic as determined by their Osmotic Pressures	i, 7
MALBOT (H.) and A. MALBOT. Action of Secondary Capryl Iodide on Trimethylamine	i, 7
MARCKWALD (W.) and A. ELLINGER. Glycolaldehydes	i, 7
MACELROY (K. P.) and W. H. KRUG. Specific Gravity of Aqueous Solutions of Acetone.	i, 7
CLAISEN (L.). Condensation of Acetaldehyde with Acetone	i, 8
BLANK (P.). Derivatives of Trimethylene Chlorobromide	i, 8
TALBOT (H. P.). Index to the Literature of Angelic and Tiglic Acids	i, 10
RAU (A.). Succinic Acid	i, 10
PERATONER (A.). Decomposition of the Ethyl Salts of some Chloro- β -ketonic Acids by Dilute Sulphuric Acid	i, 11
TANATAR (S.) and C. TCHELEBIEFF. Specific Gravity of some Isomeric Acids	i, 11
PHLOKIN (S.). Oxidation of Diallylacetic Acid by Potassium Permanganate	i, 12
MARKOVNIKOFF (V.). Action of Bromine on Closed Chain Hydrocarbons in presence of Aluminium Bromide	i, 13
MARKOVNIKOFF (V.). Suberene	i, 13
SHAW (G. E.). Hexiodobenzene	i, 14
HÄUSSERMANN (C.). Preparation of α -Trinitrotoluene	i, 14
NIETZKI (R.) and E. REHE. Dinitrochlorotoluene and the Synthesis of Azine Dyes.	i, 15
CASSIRER (H.). Orthocyano- and Orthonitro-benzyl Chloride.	i, 16
VOLPJAN (L.). Preparation of Optically Inactive Cymene from Oil of Caraway	i, 17
PERATONER (A.). Phenacetylene Diiodide	i, 18
PERATONER (A.). Phenyliodacetylene	i, 19
REVERDIN (F.) and C. DE LA HARPE. Dinitrophenol	i, 19
PAAL (C.) and A. BODEWIG. Orthonitrobenzyl Alcohol	i, 20
CIAMICIAN (G.) and P. SILBER. Derivatives of Quinol, Resorcinol, and Phloroglucinol	i, 21

	PAGE
NEMIROVSKY (A.). Isomeric Bromanilines	i, 21
REVERDIN (F.) and C. DE LA HARPE. Action of Acetic Anhydride on Dimethylaniline	i, 23
PAAL (C.) and E. LAUDENHEIMER. Orthamidobenzyl Alcohol and its Derivatives	i, 23
PESCI (L.). Methylphenylmercurammonium Hydroxide and Salts	i, 24
PERATONER (A.) and G. SIRINGO. Action of Carbonyl Chloride on Sodiophenylhydrazine	i, 24
PAAL (C.) and E. LAUDENHEIMER. Action of Carbon Bisulphide on Orthamidobenzyl Alcohol	i, 25
MARCKWALD (W.) and P. WOLFF. Diphenylguanidine	i, 25
MARCKWALD (W.). Stereoisomeric Thiosemicarbazides	i, 26
JAFFÉ (M.). Dibenзамide and Tribenzamide	i, 29
MICHELIS (W.). Seleno- and Thio-derivatives of Ethylamine	i, 30
GABRIEL (S.) and W. MICHELIS. Triamidopropane	i, 31
LANDAU (S.). Mesitylene	i, 32
ASCHAN (O.). Hydrobenzoic Acids	i, 33
DELISLE (A.) and A. SCHWALM. Organic Sulphur Compounds	i, 35
ERLENMEYER (E., jun.). Phenylpyruvic and Phenylglycidic Acids	i, 36
STEBBINS (J. H., jun.). Action of Sulphuric Acid on Quinol	i, 37
PAAL (C.) and E. LAUDENHEIMER. Synthesis of 2-Dimethylhydrindole	i, 37
GRAEBE (C.). Bidiphenylenethylene, a Red Hydrocarbon	i, 38
HENRIQUES (R.). Derivatives of 1:4-Ethoxyamidonaphthalene	i, 39
SPIEGEL (L.). Action of Phenylhydrazide on Cantharidin	i, 40
SCHUNCK (E.). Chlorophyll	i, 41
TSCHIRCH. Trichosanthin and Thallochlore	i, 42
ANGELI (A.). Affinity Coefficients of some Pyrroline and Indole Acids	i, 42
VARET (R.). Action of Piperidine and Pyridine on Haloïd Salts of Cadmium	i, 43
KNUDSEN (P.). Action of Bromine on Aldehydeollidine	i, 43
GOLENIN (A.) and A. KLEPIKOFF. Oxidation of Quinoline by Potassium Permanganate	i, 44
BISCHLER (A.). New Synthesis of Pyrazole Derivatives	i, 44
NIETZKI (R.) and A. BOSSI. Oxazine Dyes	i, 44
WITT (N. O.), E. NOELTING, and E. GRANDMOUGIN. Indazole Derivatives	i, 46
PAAL (C.) and E. FRITZWEILLER. 2-Paratolyindazole	i, 46
BISCHLER (A.) and D. BARAD. Phenometadiazine	i, 47
WOLFF (C.). Quinazolines	i, 49
TIGERSTEDT (A.). Action of Alcoholic Potash on the Anilides, &c., of α -Bromopropionic, α -Bromobutyric, and α -Bromisobutyric Acids	i, 51
BISCHOF (C. A.) and C. TRAPESONZJANZ. Monkotopiperazines	i, 53
BISCHOF (C. A.). Piperazine Group	i, 54
JOHNSON (G. S.). Organic Bases in the Juice of Flesh	i, 55
SKRAUP (Z. H.). Conversion of Cinchona Alkaloids into Isomerides	i, 56
HESSE (O.). Coca Leaves	i, 57
GRIFFITHS (A. B.). Echinochrome, a Respiratory Pigment	i, 59
GRIFFITHS (A. B.). Hermerythrin, a Respiratory Pigment in the Blood of certain Worms	i, 59
HEWLETT (R. T.). Fractional Heat Coagulation of Proteids	i, 59
VIGNON (L.). Rotatory Power of Fibroin	i, 60
GRIFFITHS (A. B.). Respiratory Globulin from the Blood of Chiton	i, 60
MIKLASCHEFFSKY (S.). Hydration of Ethylenic Hydrocarbons	i, 61
MAQUENNE (L.). Preparation of Acetylene	i, 62
MEYER (V.) and P. PETRENKO-KRITSCHENKO. Action of Bromine on Ethyl Chloride and certain Butane Derivatives	i, 62
STOKES (H. N.). Catalytic Action of Aluminium Chloride on Ethereal Silicates	i, 62
SCHÜPPHAUS (R. C.). Alcohols in Fusel Oil	i, 63
LIPPMANN (E. O. v.) and O. HAHN. Levulan	i, 63

CONTENTS.

v

	PAGE
LIPPMANN (E. O. v.). Dulcitol	i, 64
LIPPMANN (E. O. v.). Sorbitol	i, 64
MICHAUD (G.) and J. F. TRISTAN. Agavose	i, 64
WEISBERG (J.). Effect of boiling with Water on Cane-sugar and Raffinose	i, 64
TROEGER (J.). Metaldehyde and Paraldehyde	i, 64
HANTZSCH (A.). Thiocyanacetone	i, 64
MEYER (V.). Substitution in Aliphatic Acids	i, 64
GENVRESSE (P.). Method of preparing Brominated Fatty Acids	i, 65
LEPERCQ (G.). Action of Alkali Nitrites on Alkyl Salts of Brominated Fatty Acids	i, 65
FREER (P. C.). Ethyl Acetoacetate and Ethyl Salicylate	i, 66
MICHAEL (A.). Ethyl Sodacetoacetate	i, 67
HJELT (E.). Relative Velocity of Lactone-formation in the case of Bibasic γ -Hydroxy-acids	i, 71
SCHINDLER (T.). Action of Sulphuric acid on β -Trimethylethylidene- lactic acid	i, 71
WEIDEL (H.) and E. HOPPE. Mesitylic acid and Mesitonic acid	i, 72
AUWERS (K.) and H. KAUFFMANN. Stereoisomeric Derivatives of the Symmetrical Dimethylglutaric Acids	i, 72
FREUNDLER (P.). Alkyl Tartrates	i, 73
STOKES (H. N.). Action of Phosphorus Oxychlorides on Aromatic Sili- cates	i, 74
SÜDERBAUM (H. G.) and O. WIDMAN. Preparation of Orthonitrobenzyl Alcohol	i, 74
STOKES (H. N.). Benzyl Silicate	i, 74
PÁBRAM (R.) and C. GLÜCKSMANN. Behaviour of Thiocarbonates towards Phenols	i, 75
CAUSSE (H.) and C. BAYARD. Pyrogallol Antimonites	i, 75, 77
BERNTSEN (A.). Metamidodialkylorthotoluidines and their Conversion into Methylene-blue Dyes	i, 75
SEMLER (F. W.). Conversion of Tanacetoxime into 1:3:4-Cymidine	i, 78
PHILIPP (C.). Condensation Products of Amidophenols and Amidophenyl Ethers with Aldehydes and Ketones	i, 78
BISCHOFF (C. A.) and A. HAUSDÖRFER. Acidoxyl Derivatives of Di- phenylethylenediamine and Ditolythylenediamine	i, 78
TRAPESONZJANZ (C.). Derivatives of Propylenediamine and Pseudo- butylenediamine	i, 79
HAUSSER (J.) and P. T. MÜLLER. Decomposition of Diazo-compounds	i, 81
PECHMANN (H. v.). Action of Diazobenzene on Malonic Acid	i, 82
PECHMANN (H. v.). Mixed Azo-compounds	i, 84
BAMBERGER (E.) and E. WHEELWRIGHT. Action of Diazobenzene on Ethyl Acetoacetate	i, 84
ECKSTEIN (F.). Phenylhydraziodoisobutyronitrile and the Products of its Hydrolysis	i, 85
MINUNNI (G.). Condensation of β -Benzoylphenylhydrazine with Alde- hydes	i, 86
MINUNNI (G.) and G. CORSELLI. Action of Phenylhydrazine on some Isomeric Aldoximes	i, 87
MINUNNI (G.) and G. CORSELLI. Determination of the Structure of the Oximido-group in the Ethers of the Oximes	i, 87
MINUNNI (G.) and G. CORSELLI. Action of Phenylhydrazine on the Benzoyl Derivatives of some α -Aldoximes	i, 88
MINUNNI (G.). Formation of Benzonitrile from α -Benzaldoxime	i, 89
MINUNNI (G.). Isomerism of Oximes	i, 89
NOELTING (E.), E. GRANDMOUGIN, and O. MICHEL. Formation of Hydrogen Nitride (Azoimide) from Aromatic Azoimides	i, 90
MINUNNI (G.). Preparation of Benzoic Anhydride: Formation of Dehydracetic acid from Acetic Chloride	i, 92
MARKOVNIKOFF (V.). Heptanaphthene (Hexahydrobenzoic) acid	i, 93

	PAGE
MEYER (L., Jun.). Separation of Phenylidibromopropionic acid into its Optically Active Modifications	i, 93
BLACKSHEAR (C. C.). Sulphone-phthaleins	i, 94
CATHCART (W. R., Jun.) and V. MEYER. Indoxazen Group	i, 94
RUSSANOW (A.). Indoxazen Derivatives	i, 95
TÄUBER (E.). Orthodiamidodiphenyl	i, 96
CATHCART (W. R., Jun.). Oximes of Symmetrical Benzophenones	i, 97
MINUNNI (G.) and G. ORTOLEVA. Benzileoximes	i, 97
MINUNNI (G.). α -Benzilephenylhydrazine and the Oxidation of the Hydrazones	i, 97
BISCHOFF (C. A.) and A. HAUSDÖRFER. Derivatives of α - and β -Naph- thylamines containing Asymmetrical Nitrogen and Carbon Atoms	i, 98
HOSAEUS (H.). Action of β -Naphthol on Formaldehyde	i, 100
WALLACH (O.) and T. RHEINDORFF. Terpenes from Resins	i, 100
WALLACH (O.) and W. WALKER. Sesquiterpenes	i, 101
WALLACH (O.) and T. RHEINDORFF. Ethereal Oil of Paracoto Bark	i, 103
SEMMLER (F. W.). Essential Oil of Garlic (<i>Allium sativum</i>)	i, 103
SEMMLER (F. W.). Essential Oil of Onion (<i>Allium cepa</i>)	i, 104
WALLACH (O.) and M. KUTHE. Menthylamine	i, 105
WALLACH (O.). Constituents of Oil of Thuja	i, 105
SEMMLER (F. W.). Camphors containing the Group $\text{CO}\cdot\text{CH}_3$	i, 107
ERRERA (G.). Campholamine	i, 108
CAZENEUVE (P.). Derivatives of Amethylcamphonitroketone	i, 109
CAZENEUVE (P.). Tinctorial Properties of Amethylcamphonitroketone	i, 110
LIPPMANN (E. O. v.). Coniferin	i, 110
GRASSI-CRISTALDI (G.). Reduction Products of Santonins, Santonone, and Isosantonone	i, 110
KLEIN (J.). Santonin	i, 111, 112
MOHRBERG (C.). Cephalanthin	i, 112
PHIPSON (T. L.). Identity of Cascarin and Rhamnoxanthin	i, 113
MERLING (G.). Action of Hydrogen Peroxide on Piperidene Bases	i, 113
WEIDEL (H.) and J. HOFF. Non-nitrogenous Acids derived from Pyr- idinecarboxylic acids	i, 114
DECKER (H.). Some Ammonium Compounds	i, 115
WALLACH (O.). Bases from Polei Oil	i, 115
GRIMAUX (E.). Quinine Double Salts	i, 115
FREUND (M.). Hydrastine	i, 116
PARTHEIL (A.). Cytisine and Ulexine	i, 119
GUSTAVSON (G.). Action of Stannic Chloride on Halogen Derivatives of Methane	i, 121
ANSCHÜTZ (R.). Preparation of Pure Chloroform from Salicylide-chloro- form	i, 121
LOSSEN (W.). Preparation of Silver Acetylde from Acetylenedicarboxylic acid	i, 121
TROGER (J.). Action of Hydrogen Chloride and Hydrogen Bromide on liquid α -Dichlorethyl Cyanide	i, 121
VERNON (H. M.). Reactions of Ferric Salts with Thiocyanates	i, 122
GRIGOROVITCH (A.) and D. PAVLOFF. Action of Acid Chlorides on Zinc Ethide	i, 124
SUNDWIK (E. E.). Psyllostearyl Alcohol	i, 125
STONE (W. E.). Synthesis of Sugars	i, 125
JACOBI (H.). Biotation and Hydrazone Formation of some Sugars	i, 125
SCHIFFERER (A.). Non-crystallisable Products of the Action of Diastase on Starch	i, 127
WINTERSTEIN (E.). Action of Dilute Alkalis and Acids on Cellulose	i, 127
WINTERSTEIN (E.). Vegetable Amyloid	i, 127
WINTERSTEIN (E.). Parent Substance of Wood-gum	i, 128
RUDNEW (W.). Molecular Compounds of Amines	i, 128
ANDREOCCI (A.). Derivatives of Urethane	i, 128
EVANS (P.). Condensation of β -Diketones with Carbamide and Thio- carbamide	i, 129

	PAGE
SEMMLER (F. W.). Derivatives of Ketopentamethylene and Keto-hexamethylene	i, 129
KURILOFF (V.). Products of the Dry Distillation of Birch Bark	i, 131
RUSANOFF (A.). Preparation of Chloracetic acid	i, 131
FOERSTER (F.). Compound of Copper Acetate with Ammonia and with Pyridine	i, 131
DRECHSEL (E.). Behaviour of α -Amidopropionic acid at High Temperatures	i, 132
MICHAEL (A.) and O. SCHULTESS. Crotonic acids and their Derivatives	i, 132
MICHAEL (A.). Formation of Solid Crotonic acids by the Reduction of α -Isobromo- and α -Isochloro-crotonic acids	i, 134
MICHAEL (Mrs. H. A.). Addition of Bromine and Chlorine to Solid Crotonic acid	i, 134
WISLICENUS (J.). Brom-additive Products of Angelic and Tiglic acids	i, 135
KONDAKOFF (I.). Constitution of Angelic and Tiglic acids	i, 141
OTTO (R.) and J. TRÖGER. Constitution of Glyoxylic acid	i, 141
LOSSEN (W.). Dibromosuccinic acids	i, 142
MICHAEL (A.) and C. C. MAISCH. Action of Sodium Ethoxide on Ethyl Dibromosuccinate	i, 142
MICHAEL (A.) and G. TISSOT. Addition of Chlorine to Polybasic Unsaturated Fatty Acids	i, 142
MULLER (T.). Action of Chlorides of Bibasic Acids on Ethyl Sodioeyanacetate	i, 143
MICHAEL (A.). Addition of Bromine to Acetylenedicarboxylic acid and its Ethyl Salt	i, 144
MICHAEL (A.). Comparison of Experimental Results with the Theoretical Conclusions of the Van't Hoff-Wislicenus Hypothesis	i, 145
BRUNNER (K.). Synthesis of Isomalic acid	i, 145
MICHAEL (A.) and G. TISSOT. Homologues of Malic acid	i, 146
WISLICENUS (W.) and A. JENSEN. Ethyl Oxalacetate	i, 146
SMITH (W. S.). Optical Isomerides of d-Mannoheptonic acid, d-Mannoheptose, and Perseitol	i, 147
HARTMANN (G.). Derivatives of d-Mannoheptonic acid	i, 148
REINBRECHT (O.). Lactosecarboxylic and Maltosecarboxylic acids	i, 148
MATIGNON (C.). Hydurilic acid	i, 149
WILLGERODT (C.). Aromatic Iodochlorides, Iodosobenzene, and Iodoxybenzene	i, 149
KIJNER (N.). Hydrogenation of Benzene	i, 150
ERDMANN (H.). Sandmeyer's Reaction and Preparation of Orthochlorotoluene	i, 150
SPINDLER (E.). Heptanaphthene from Caucasian Naphtha	i, 151
HARTMANN (C.) and L. GATTERMANN. Hydrolysis of Phenolic Ethers and of Etheral Salts by means of Aluminium Chloride	i, 152
CAZENEUVE (P.). Propylamidophenol from Camphor	i, 152
FRIEDMANN (A.) and L. GATTERMANN. Action of Thiocarbimides on Aromatic Hydrocarbons	i, 153
TUST (K.) and L. GATTERMANN. Action of Phenol Ethers on Thiocarbimides	i, 154
PECHMANN (H. v.). Aromatic Diazo-compounds	i, 154
THIEME (B.). Salts and Derivatives of Phenylhydrazine	i, 154
MEYER (P.). Bromination of Phenylhydrazine	i, 155
PURGOTTI (A.). Paranitrophenylhydrazine	i, 155
WISLICENUS (W.). Synthesis of Formazyl Compounds by the Action of Diazobenzene on Hydrazones	i, 156
BAMBERGER (E.). Action of Diazobenzene on β -Ketonic Acids	i, 156
BAMBERGER (E.) and J. LORENZEN. Formazyl Methyl Ketone	i, 157
SÖDERBAUM (H. G.). Behaviour of certain Aromatic Isonitrosoketones towards Acetic Anhydride and Acetic Chloride	i, 159
ERDMANN (H.). Preparation and Nitration of Orthochlorobenzaldehyde	i, 160
STOCKHAUSEN (F.) and L. GATTERMANN. Aluminium Chloride and Nitro-compounds	i, 161

	PAGE
CLAUS (A.). Aromatic Alkyl Ketones	i, 162
STOCKHAUSEN (F.) and L. GATTERMANN. Aromatic Ketones	i, 163
USPENSKY (N. N.). Azoxybenzoic acids	i, 164
USPENSKY (N. N.). Action of Phosphorus Pentachloride on Azo- and Azoxy-benzoic acids	i, 165
ANSCHÜTZ (R.). Salicylide	i, 165
ERLENMEYER (E., Jun.). New Phenylamidolactic acid from Glycocine and Benzaldehyde	i, 166
WEGSCHEIDER (R.). Methylation of Opianic acid	i, 167
SCHIFF (H.). Anilide of Gallic acid	i, 167
OTTO (R.) and J. TRÖGER. Synthesis of Symmetrical Diphenylsulphone-acetone by means of Symmetrical Dichloracetone	i, 167
LIMPRICHT (H.). Nitrososulphonic acids	i, 168
HINSBERG (O.). Benzenesulphonamides	i, 168
BRUNCK (R.). Thienylindole, α -Naphthindole, and some Bromo-derivatives of Indoles	i, 168
ABENIUS (P. W.) and H. G. SÖDERBAUM. Aromatic Tetraketones	i, 169
MICHEL (O.) and E. GRANDMOUGIN. Acetyl Derivatives of 2 : 1-Amidonaphthol	i, 171
WENDT (G.). Methylnaphthalenes	i, 171
ABEL (J.). Condensation of Formaldehyde with Naphthols	i, 172
RUSANOFF (A.). Condensation of Chloral Hydrate with Naphthols	i, 173
BALBIANO (L.). Oxidation of Camphoric acid	i, 174
SPINDLER (E.). Action of Hydriodic acid on Piperidine	i, 174
VARET (R.). Action of Piperidine on Haloid Salts of Mercury	i, 174
AUERBACH (F.). New Collidine	i, 175
AUERBACH (F.). Pilocolinecarboxylic acid	i, 176
PERLMUTTER (A.). Action of Nascent Hydrogen on Quinolic acid	i, 176
ROSER (W.). Constitution of the so-called Quinoline Ammonium Bases	i, 177
MAGNANINI (G.) and M. SCHEIDT. Action of Benzaldehyde on the Ammoniacal Derivatives of Dehydrodiacetyllevulinic acid	i, 177
MARCHETTI (G.). Reduction of 1 : 4 : 5-Phenylmethylethylpyrazole : 1 : 3 : 5-Phenyldimethylpyrazole	i, 177
MARCHETTI (G.). Reduction of 1 : 3 : 5-Phenyldimethylpyrazole	i, 178
SEVERINI (O.). Constitution of Acetyl-1-phenylpyrazole	i, 179
MARCHETTI (G.). Pyrazole Derivatives	i, 179
ROTHENBURG (R. v.). Pyrazolone	i, 180
GOLDSCHMIEDT (G.) and F. SCHRANZHOFFER. Papaverinic acid	i, 180
GOLDSCHMIEDT (G.). Laudanine	i, 181
HEMMELMAYR (F. v.). Meconinemethyl Phenyl Ketone	i, 181
CLAUS (A.). Cinchona Alkaloids	i, 181
PUM (G.). Molecular Transformation of Cinchonine	i, 181
LIEBERMANN (C.). Coca Leaves	i, 182
HILLER-BOMBIEN (O.). Geoffroya Barks	i, 182
GRIFFITHS (A. B.). Ptomaines from the Urine in Erysipelas and Puerperal Fever	i, 183
VIGNON (L.). Preparation and Properties of Fibroin	i, 183
CHURCH (A. H.). Turacin	i, 184
NICKEL (E.). Graphochemistry of Compounds $C_nH_mO_p$	i, 185
BESSON (A.). Carbon Chloriodide	i, 185
KRÜSS (G.) and H. MORAHT. Reaction between Ferric Salts and Soluble Thiocyanates	i, 185
MESLANS (M.). Action of Anhydrous Hydrogen Fluoride on Alcohols	i, 186
KANONNIKOFF (I. I.). Rotatory Power of Sugars	i, 186
PANORMOFF (A.). Formation of Ethereal Salts of Benzoic acid from Alcohols and Carbohydrates	i, 186
RÖHMANN (F.). Conversion of Starch into Sugar by means of Blood Serum	i, 187
EFFRONT (J.). Chemical Conditions of the Action of Diastases	i, 187
FISCHER (E.). Amidoacetaldehyde (Ethanalamine)	i, 187

	PAGE
TCHERNIAC (J.). Thiocyanacetone	i, 188
MINUNNI (G.). Constitution of Aliphatic Isomeric Oximes	i, 188
ANSCHÜTZ (R.) and W. O. EMERY. Perchlorethyl Chloroformate and Trichloromethyl Trichloracetate.	i, 188
FITTIG (R.). Brom-additive Products of Angelic and Tiglic acids	i, 188
SHIMOYAMA (Y.). New Unsaturated Fatty Acid	i, 189
FITTIG (R.). Intramolecular Changes in Unsaturated Acids	i, 189
ANSCHÜTZ (R.) and F. BIERNAX. Diglycollic acid and Thiodiglycollic acid	i, 191
TANATAR (S.). Action of Water on Bromosuccinic acid	i, 192
SELIVANOFF (T.). Mixed Anhydrides of Hypochlorous acid and Analogous Acids	i, 192
ANDERLINI (F.) and E. BORISI. Condensation of Ethyl Formate and Succinate	i, 192
ANSCHÜTZ (R.) and E. PARLATO. Ethyl Oxomalonate	i, 193
TANATAR (S.). Isomerism of Fumaric and Maleic acids	i, 193
SEMENOFF (V.). Homologues of Citraconic, Itaconic, and Mesaconic acids	i, 194
FRIEDEL (C.). Stereochemical Notation	i, 195
SCHULZE (E.). Constitution of Leucine	i, 195
FILETI (M.) and A. CANTALUPO. Preparation of Zinc Ethide.	i, 196
KONOVALOFF (M.). Derivatives of Nononaphthene.	i, 196
ANGELI (A.). Action of Nitric and Nitrous acids on certain Organic Substances	i, 196
SCHUNCK (E.) and L. MARCHLEWSKI. Action of Hydrogen Peroxide on Aniline	i, 197
MICHAEL (R.). Paraxylylidine	i, 198
LELLMANN (E.) and N. MAYER. Some Nitro- and Amido-benzylated Bases	i, 198
CAZENEUVE (P.). Propylamidophenol and its Acetyl Derivatives	i, 199
KEHRMANN (F.) and J. MESSINGER. Alkyl Orthodiamines	i, 199
BAMBERGER (E.) and B. BERLÉ. Dibenzylidiamidoethylene	i, 200
WOHL (A.). Diazobenzene	i, 200
NEUBERT (C.). Azo- and Hydrazo-benzyl Alcohols.	i, 200
LELLMANN (E.) and N. MAYER. Intramolecular Formation of the Azo-group.	i, 201
NIEMENTOWSKI (S.). Diazoamido-compounds.	i, 201
NOELTING (E.) and O. MICHEL. Conversion of Amines into Diazoimides by means of Azoimide.	i, 202
NOELTING (E.) and O. MICHEL. Action of Diazo-compounds on Hydrazines.	i, 202
BECKMANN (E.) and E. FELLRATH. Action of Phenylcarbimide on Benzylbenzaloxime	i, 203
HOLLEMAN (A. F.). Action of Amines and Ammonia on the Dinitrosoacetyls	i, 205
TIVOLI (D.). Phenylanilicyanamide and β -Diphenylsemithiocarbazide	i, 206
HANTZSCH (A.). Stereochemistry of Unsymmetrical Hydrazones	i, 207
OVERTON (B.). Stereochemical Phenyl- and Diphenyl-hydrazones	i, 208
ASCHAN (O.). Hexahydrobenzoic acid	i, 209
ASCHAN (O.). Acids from Baku Petroleum	i, 209
PAAL (C.) and E. FRITZWEILER. Orthonitrometamidobenzoic acid.	i, 209
KRÜCKEBERG (F.). Ethyl Azobenzenecyanacetate	i, 210
DIERBACH (R.). Anilidosalicylic acid	i, 211
FILETI (M.). Stereoisomeric Isopropylphenylglycollic acids	i, 212
FILETI (M.) and E. CAROLA. Derivatives of Homoterephthalic acid	i, 212
ADOLPHI (W.). Chebulic acid	i, 212
MARCKWALD (W.) and A. ELLINGER. A Derivative of Amidoacetal	i, 213
MAZZARA (G.) and E. LEONARDI. Acetylnitrocarbazole	i, 213
DIANIN (A.). Condensation of Ketones with Phenols	i, 214
ZENONI (M.). Condensation Products of Dimethylresorcinol and Methylresorcinol with the Nitrobenzaldehydes	i, 216

	PAGE
SCHÖPPF (M.). Xanthone Derivatives and Orthoeresotic Anhydride	i, 217
DREHER (E.) and S. V. KOSTANECKI. Constitution of Monhydroxy-xanthenes	i, 217
BAUMEISTER (W.). Preparation of Hydroxyxanthenes from the Salols of Polyhydric Phenols	i, 218
SMITH (A.). Condensations with Potassium Cyanide	i, 219
SMITH (A.). Condensation of Acetone with Benzoïn by means of Potassium Cyanide	i, 219
MEYER (R.) and E. SAUL. The Fluoresceïn Group	i, 220
ZINCKE (T.). Action of Bleaching Powder and of Hypochlorous acid on Quinones	i, 220
ROSENBERG (N.). Derivatives of the β -Naphtholcarboxylic acid melting at 216°	i, 221
CONRAD (M.) and W. FISCHER. α -Naphtholsulphonic acids	i, 221
WOLFF (W.). Dinaphthoxanthen (Methylenedinaphthylene Oxide)	i, 222
BOUCHARDAT (G.) and J. LAFONT. Action of Sulphuric acid on Citrene	i, 223
ANTHOINE. Crystalline Dihydrochloride from Eucalyptus Oil	i, 223
LONG (J. H.). American Menthol	i, 223
NEGVOVOROFF (A.). Amine from Dextromenthone	i, 224
HIRSCHSOHN (E.). Occurrence of Bornyl Acetate in the Ethereal Oils of <i>Abies sibirica</i> and <i>Abies pectinata</i>	i, 224
OSTERLE (O.). Guttapercha	i, 224
SCHALL (C.). Brazilin Methyl Ether	i, 225
POLECK (T.). Jalapin	i, 225
RIEDEL (J. D.). Names of New Remedies	i, 225
MOISSAN (H.). Opium Smoke	i, 226
GAUTIER (A.). Tobacco Smoke	i, 226
ZANETTI (C. U.). Constitution of the Methylpyrrolines	i, 226
JENNSTEDT (M.). Action of Propyl Alcohol on Pyrroline	i, 226
FERRATINI (A.). Trimethyltetrahydroquinoline	i, 227
FERRATINI (A.). Tetrahydroisoquinoline	i, 227
GABRIEL (S.) and A. NEUMANN. Synthesis of Isoquinoline Derivatives	i, 228
TCHERNIAC (J.). Preparation and Properties of Methyloxythiazole	i, 228
KNORR (L.). The Pyrazoline Reaction	i, 229
KNORR (L.) and P. DUDEN. Pyrazole Derivatives from Unsaturated Acids and Hydrazines	i, 229
KNORR (L.) and P. DUDEN. Isomerism of the Diphenylpyrazones and of the Pyrazole Derivatives from Ethyl Benzoylacetate and Ethyl Benzalacetate	i, 230
DUDEN (P.). Pyrazoles from Unsaturated Acids and Hydrazines	i, 231
NEUMANN (G.). Action of Hydriodic acid on Cinchonidine	i, 231
AHRENS (F. B.). Sparteine	i, 232
SANSONI (L.). Behaviour of Hydrochloric acid to Albumin in relation to the Chemical Investigation of Gastric Juice	i, 233
KÜHNE (W.). Albumoses and Peptone	i, 233
KOSSEL (A.) and F. FREYTAG. Certain Chemical Constituents of the Medulla of Nerve	i, 234
SCHÜTZENBERGER (P.). Chemical Constitution of Peptones	i, 235
GRIFFITHS (A. B.). γ -Achromoglobin, a New Respiratory Globulin	i, 236
GRIFFITHS (A. B.). Pigments of Lepidoptera	i, 236
LENGFELD (F.) and E. O'NEILL. Californian Petroleum	i, 237
GRINER (G.). Some Cases of Isomerism in the C_6 Series	i, 237
BESSON (A.). Decomposition of Chloroform in the presence of Iodine	i, 242
BEWAD (I.). Synthesis of Mononitroparaffins	i, 242
LOBRY DE BRUYN (C. A.). Methyl and Ethyl Alcohol as Solvents	i, 244
COUTURIER (F.). Pinacone and its Derivatives	i, 244
RAISSONNIER (L.). Bye-products of the Action of Sodium Hydroxide on Glycerol	i, 246
COMBES (A.) and LE BEL. Supposed Secondary Hexyl Alcohol from Mannitol	i, 246

	PAGE
FRANCHIMONT (A. P. N.). Pentacetyl Derivatives of Glucose . . .	i, 246
HANRIOT and C. RICHET. Chloralose, a Derivative of Chloral and its Physiological Properties	i, 247
DE CHALMOT (G.). Soluble Pentoses in Plants	i, 247
BERTRAND (G.). Xylose	i, 248
BAUER (R. W.). Sugar from Pear Pectose	i, 248
WINTERSTEIN (E.). Inversion of Some Carbohydrates	i, 249
CHANCEL (F.). Preparation and Purification of the Propylamines . . .	i, 249
MICHAELIS (A.) and O. STORBECK. Thionyl-diethylhydrazone	i, 249
WALDEN (P.). Alleged Optical Activity of Chlorofumaric acid: an Active Chlorosuccinic acid.	i, 250
ELBS (K.). Electrolysis of Trichloroacetic acid	i, 250
BISCHOFF (C. A.) and P. WALDEN. Glycolide and its Homologues. . .	i, 250
LUMIÈRE (A.) and A. SEYEWETZ. Action of Potassium Permanganate on Organic Acids	i, 251
BRÜHL (J. W.) and R. BRAUNSCHWEIG. Asymmetrical Dicarboxylic acids .	i, 251
MEISTER (H.). Metahydroxyvitic acid	i, 252
AUWERS (K.). Pentanetetracarboxylic acid; Synthesis of Pentamethylene Derivatives	i, 253
CHANCEL (F.). D propylcarbamide and Dipropylthiocarbamide	i, 253
KEHRER (E. A.) and W. KLEBERG. β -Furfurallevulinic acid: a New Synthesis of Coumarone Derivatives	i, 254
BAEYER (A.). Hydro-derivatives of Benzene	i, 255
LOBRY DE BRUYN (C. A.). Preparation of Orthodinitrobenzene	i, 256
OTTO (R.). Reactions of Phenyl Iododichloride and Iodosobenzene . .	i, 256
WILLGERODT (C.). Aromatic Iododichlorides, Iodoso- and Iodoxy-com- pounds	i, 256
LEVY (L.). Titanium	i, 257
BAEYER (A.). Synthesis of Dihydrocymene	i, 258
COUSIN (H.). Ethers of Homocatechol	i, 258
ZINCKE (T.). Action of Chlorine on Phenols	i, 259
ANGELI (A.). Action of Nitrous acid on Isosafrole	i, 261
ANGELI (A.) and P. BARTOLOTTI. Action of Nitrous acid on Isoapiole .	i, 263
GIUSTINIANI (E.). Compounds of Malic and Fumaric acids with Aro- matic Amines	i, 264
TAFEL (J.) and I. VOGEL. Action of Carbamide on Nitrosamines	i, 265
WEINBERG (A.). Paramidoalkylorthotolidine	i, 265
IKUTA (M.). Metamidophenol and its Derivatives	i, 265
FISCHER (O.) and O. HEILER. Oxidation Products of Orthodiamines . .	i, 266
ZANETTI (C. U.). Products of the Reduction of Orthophenylenediaceto- nitrite.	i, 267
SCHJERNING (H.). Compounds of Phenylhydrazine with Metallic Salts .	i, 267
DUPONT (J.). Preparation of Methylbenzoic Anilide	i, 268
HOOGWERFF (S.) and W. A. VAN DORP. Orthocyanotenzoic acid	i, 268
ZALOZIECKI (R.). Acids occurring in Petroleum	i, 268
LIEBERMANN (C.). Specific Rotatory Power of the Phenyl-dibromoprop ionic acids.	i, 268
FORTE (O.). Derivatives of Cresolglycollic acids	i, 269
BIÉTRIX (A.). Dibromogallie acid and its Salts	i, 269
OTTO (R.) and J. TRÖGER. Constitution of the Iodides of Aromatic Sulphonic acids	i, 269
HAUSSER (J.). Cryoscopic Studies in the Benzene Series.	i, 270
OTTO (R.). Preparation of Pure Ethyl Benzenesulphinate and Ethyl Paratoluenesulphinate	i, 270
HEUMANN (K.) and C. BACHOFEN. Behaviour of Indigo when heated with Alkalis	i, 270
ELBS (K.). Derivatives of Diphenyltrichlorethane and their Conversion into Stilbene	i, 271
HARGELE (E.). Condensation Products of Amidophenols	i, 273
LINEBARGER (C. E.). Solubility of Diphenylmethane in Benzene	i, 273

	PAGE
FRIEDLÄNDER (P.). Phenolphthaleïn	i, 273
CARO (N.). Trihydroxyaurin from Catechol	i, 274
MONNET (P.). Anisolines.	i, 274
SACHS (J.). Substitution Products of the Naphthyl Ethers	i, 274
MEYER (R.). Compounds of Phthalic acid and Phenols	i, 275
NIETZKI (R.) and R. ZEHNTER. Benzeneazonaphthalene and Toluene- azonaphthalene	i, 275
OTTO (R.), A. RÖSSING, and J. TRÖGER. Sulphonic Derivatives of Naph- thalene	i, 276
BOUVEAULT (L.). Constitution of Camphor and Oil of Turpentine, and of their Principal Derivatives	i, 276
ANGELI (A.). Novel Conversion of Camphor into Camphoric acid	i, 277
MANASSE (O.). Conversion of Nitrosocamphor into Camphoric Imide : Camphordioximes	i, 277
BRÜHL (J. W.) and R. BRAUNSCHWEIG. Terpenes and their Derivatives	i, 277
SPIEGEL (L.). Action of Phenylhydrazine on Cantharidin	i, 278
DECKER (H.). Action of Alkalis on Pyridine Alkyl Iodides and Similar Bases	i, 279
VARET (R.). Combination of Quinoline with Silver Haloids	i, 279
SCHAD (P.). Synthesis of Ring Compounds from Benzene Derivatives with Open Side Chains	i, 279
MAQUENNE. Glyoxalinedicarboxylic acids	i, 281
BUCHNER (E.) and M. FRITSCH. 4-Phenylpyrazole.	i, 281
BUCHNER (E.) and H. DESSAUER. 5-Phenylpyrazole	i, 282
FISCHER (O.) and E. FRANCK. Ammonium Derivatives of Azines	i, 282
FISCHER (O.) and A. JUNK. Naphthazines	i, 283
FISCHER (O.). Orthodiamine Derivatives	i, 283
PINNER (A.). Constitution of Nicotine	i, 286
TAFEL (J.). Oxidation of Strychnine	i, 287
CIAMICIAN (G.) and P. SILBER. Pseudopelletierine.	i, 287
KRAKOW (N. P.). Amyloid Substance	i, 288
FLEURENT (E.). Combination of Cuprous Cyanide with Alkali Cyanides	i, 289
BROCHE (C.). Tribromacetonitrile	i, 289
GLADSTONE (J. H.). Reactions of Ferric Salts with Thiocyanates	i, 289
VERNON (H. M.). Reaction of Ferric Salts with Thiocyanates.	i, 290
NORDENSKJÖLD (O.). Thiocyanates of Chromammonium Compounds	i, 290
DE FORCRAND (R.). Hydrates of Alcohols	i, 291
FISCHER (E.). Adonitol, a New Pentitol.	i, 291
WOHL (A.). Dextrose	i, 292
STONE (W. E.) and W. H. TEST. Xylose.	i, 294
BÉCHAMP (A.). Gum Arabic	i, 294
FLINT (E. R.) and B. TOLLENS. Oxycellulose and Bornesitol	i, 295
CROSS (C. F.) and E. J. BEVAN. Explosive Nitrates from the Jute Fibre BERG (A.). Chlorine Derivatives of Propylamines, Benzylamines, Anil- ine, and Paratoluidine	i, 296
CHANCEL (F.). Dipropylcyanamide and Dipropylcarbodiimide.	i, 297
NOTHNAGEL (G.). Muscarine	i, 297
MOSCHATO (H.) and B. TOLLENS. Additive Products and Compounds of Hexamethylenamine	i, 298
CLAUS (A.). Isomerism of Asymmetrical Hydrazines	i, 299
CURTIS (T.). Hydrazine Derivatives	i, 299
FISCHER (E.). Amidoacetaldehyde	i, 300
ZECCINI (F.). Molecular Weight of Metaldehyde	i, 301
BÉHAL (A.) and E. CHOAY. Derivatives of Chloral	i, 301
KOENIGS (W.) and E. WAGSTAFFE. Condensation of Chloral and Butyl- chloral with Acetone and Acetophenone	i, 302
FRITSCH (P.). Chlorination of Acetone	i, 303
BEHREND (R.) and J. SCHMITZ. Action of Nitric acid on Acetone	i, 303
ANSCHÜTZ (R.) and W. MONTFORT. Formation of Phoronic acid from Phorone	i, 304

	PAGE
BALESTRA (E.). New Mercurammonium Salts	i, 304
SELIVANOFF (T.). Mixed Anhydrides of Hypochlorous and analogous acids	i, 305
BARTHE (L.). Synthesis with the aid of Ethylic Cyanacetate and Ethylic Cyanosuccinate	i, 305
GROSSMANN (O. V.). Oxidation Products of Behenic acid	i, 305
ANSCHÜTZ (R.). Heintz's Glycollide	i, 306
GENVRESSE (P.). Ethylic Carbacetosuccinate	i, 306
ANGELI (A.). Action of Iodic acid on Malonic acid	i, 307
BRÜHL (J. W.) and R. BRAUNSCHWEIG. Ethereal Salts of Pyrotartaric acid	i, 307
BÜCHNER (O.). Trichloropyruvic acid	i, 308
LOVÉN (J. M.). Action of Hydrogen Sulphide on Pyruvic acid	i, 308
WENGER (W. H.). Solubility of Cream of Tartar in Dilute Alcohol	i, 308
SCHULZE (E.) and A. LIKIERNIK. Constitution of Leucine	i, 309
WULFF (C.). Nuclein Bases	i, 309
ANGELI (A.). Oxidation of Substances containing the Group $C_2N_2O_2$	i, 310
LENGFELD (F.) and J. STIEGLITZ. Nitrogen Halogen Compounds	i, 310
WISSELL (L. v.) and B. TOLLENS. Furfuryl alcohol and its Derivatives	i, 311
HILL (H. B.) and W. L. JENNINGS. Methylfurfuraldehyde and Methylpyromucic acid	i, 311
SAUNDERS (C. E.). Derivatives of Pyromucamide	i, 313
HILL (H. B.) and W. S. HENDRIXSON. Chlorosulphopyromucic acids	i, 313
BURNS (P. S.). Reactions of Dimolecular Nitriles	i, 314
STOKES (H. N.). Amidophosphoric acid	i, 315
DE FORCRAND. Alkali Phenoxides	i, 316
PELLACANI (F.). Derivatives of Dibromothymol	i, 316
ZINCKE (T.). Action of Chlorine on Phenols	i, 317
ZINCKE (T.) and O. FUCHS. Conversion of the Ketochlorides of Resorcinol and Orcinol into Pentene Derivatives	i, 318
BÉHAL (A.) and E. CHOAY. Creosotes and Guaiacol	i, 320
CLARK (T. H.). Additive Products of Benzoquinone and Toluquinone	i, 320
GRINDLEY (H. S.) and C. L. JACKSON. Derivatives of Chloranil	i, 322
PICCININI (A.) and G. RUSPAGGIARI. Mercuranilido-compounds	i, 322
PRUD'HOMME. Direct Conversion of Aniline into Nitrobenzene	i, 323
BAMBERGER (E.) and F. MEIMBERG. Direct Conversion of Aniline into Nitrobenzene	i, 323
RUDERT (P.). Action of Phosphorus Oxychloride and of Phosphorus Trichloride on Aromatic Amines	i, 323
KEHRMANN (F.) and J. MESSINGER. Oxidation Products of Alkyl Derivatives of Orthodiamines	i, 324
KÜHLING (O.). Interaction of Orthamidotolylamine and Alloxan Derivatives	i, 324
REMSER (I.) and P. J. DASHIELL. Decomposition of Diazo-compounds	i, 325
BAMBERGER and L. STORCH. Behaviour of Diazobenzene towards Potassium Ferricyanide	i, 326
BAMBERGER (E.) and K. LANDSTEINER. Behaviour of Diazobenzene towards Potassium Permanganate	i, 327
JACOBSEN (P.), F. C. FERTSCH, and W. FISCHER. Reduction Products of Azo-compounds	i, 327
JACOBSEN (P.), F. HENRICH, and J. KLEIN. Reduction Products of Azo-compounds	i, 327
JACOBSEN (P.). Reduction Products of Azo-compounds	i, 327
PURGOTTI (A.). Action of Sodium Sulphide on Orthodiazophenol Chloride	i, 330
HALLER (A.) and A. GUYOT. Diazoamidobenzene and Paradiazotoluene Benzoates	i, 331
STRACHE (H.) and S. IRTZER. Oxidation of Acid Hydrazides by Fehling's Solution	i, 331
EINHORN (A.) and F. K. DE NORWALL. Action of Bromine on Dihydrobenzaloxime	i, 332

	PAGE
PINNOW (J.). Action of Benzenesulphonic Chloride on Amidoximes	i, 332
ROSENSTIEHL (A.). Acid Salts and Constitution of Rosanilines	i, 332
WEIGLE (A.). Spectrophotometric Investigation of the Salts of Aromatic Bases	i, 333
FISCHER (O.) and E. HEPP. The Induline Group	i, 333
SCHRAUBE (C.) and E. ROMIG. Isoparatolylrosinduline	i, 339
FRITSCH (P.). Acetylphenylcarbamide	i, 340
CLAUS (A.). Constitution of Thiocarbamide and Phenylthiobiuret	i, 341
BLANK (A.). Action of Diazobenzene Chloride on α -Hydroxyvitic acid	i, 341
EINHORN (A.). Dihydrobenzaldehyde	i, 341
MÜLLER (R.). α -Phenylcinnamic acid	i, 341
PULVERMACHER (G.). Phenyl- α -hydroxyerotic acid	i, 342
POMERANZ (C.). Bergapten	i, 342
TRIMBLE (H.). Chestnut Bark Tannin	i, 343
BIÉTRIX (A.). Derivatives of Gallic acid	i, 343
DASHIELL (P. J.). Parethoxyorthotoluenesulphonic acid	i, 343
OTTO (R.) and A. RÖSSING. Etheral Sulphinates	i, 343
OTTO (R.) and G. ZUSCHLAG. Chemical Behaviour of Etheral Salts of Sulphinic acids	i, 344
ZINCKE (T.) and H. GÜNTHER. Conversion of Benzene Derivatives into Indene Derivatives	i, 344
GABRIEL (S.) and A. NEUMANN. Derivatives of Phthalazine and Isoindole	i, 346
JUILLARD (P.). Indigotintrisulphonic and Indigotintetrasulphonic acids	i, 348
MAZZARA (A.) and E. LEONARDI. Carbazole	i, 349
VOLPI (A.). A New Acridine and an Acridylpropionic acid	i, 350
KLAGES (A.) and E. KNOEVENAGEL. Formation of Stilbene	i, 350
GILL (A. H.). Condensation of Orthochlorobenzal Chloride by means of Metals	i, 351
FOX (F.). Condensation of Orthochlorobenzotrichloride by means of Metals	i, 351
SELCH (E.). Diresorcinol	i, 352
KNOEVENAGEL (E.) and R. WEISSGERBER. Stereoisomeric Benzamarones	i, 352
KNOEVENAGEL (E.) and R. WEISSGERBER. Benzylidenedeoxybenzoïn	i, 353
KLINGEMANN (F.). Condensation of Benzaldehyde with Deoxybenzoïn	i, 353
KEMPINSKI (S.). Condensation of Chlorobenzile with Phenol and with Mono- and Di-methylaniline	i, 354
PURGOTTI (A.). Reduction of Benzilehydrazone	i, 354
AUWERS (K.) and M. SIEGFELD. Benzileoximes	i, 354
CLAUS (A.). Oximes	i, 355
ANGELI (A.). Compounds containing the Group CNO	i, 355
HOSAEUS (H.). Hydroxynaphthoic acid	i, 355
ZINCKE (T.). Azines and Eurhodines obtained from Dihydroxydiketotetrahydronaphthalene	i, 356
LINEBARGER (C. E.). Paranthracene	i, 357
LINEBARGER (C. E.). Friedel-Crafts Reaction in the Anthracene Series	i, 358
STSCHUKAREFF (A.). Valency of the Dextroterpenes in Russian Turpentine	i, 358
BOUCHARDET and OLIVERO. Action of Acetic and Formic acids on Terbenzene	i, 358
BAEYER (A.). Orientation in the Terpene Series	i, 359
CLAISEN (L.). Hydroxymethylene Compounds	i, 360
ETARD (A.). Aldehydes from Terpenes	i, 360
KOENIGS (W.) and A. EPPENS. Camphorone	i, 361
HALLER (A.). Function of Camphoric acid	i, 361
CAZENEUVE (P.). Action of Alkali Alkylloxides on Camphoric Anhydride and other Anhydrides	i, 362
KOENIGS (W.) and J. HOERLIN. Sulphocamphylic acid	i, 363

	PAGE
KLEIN (J.). Santoninoxime and Santoninoximic acids	i, 363
CANNIZZARO (S.). Klein's View of the Constitution of Santonin	i, 364
COSSA (A.). New Series of Basic Platinum Compounds	i, 364
DECKER (H.). So-called Quinolinium Bases	i, 365
CLAUS (A.) and K. HOFFMANN. Nitro-derivatives of Isoquinoline	i, 366
FRITSCH (P.). Synthesis of Isocumarin and Isoquinoline Derivatives	i, 366
ROTHENBURG (R. v.). Pyrazolone and some of its Derivatives	i, 367
WALKER (C.). Condensation Products of the Hydrazides of Ethylic Aceto- acetate and Oxalacetate	i, 367
ROTHENBURG (R. v.). Benzo-3-phenylpyridazolone	i, 368
WARMINGTON (E.). Phenyluracil and its Analogues	i, 369
MICHAELIS (A.) and R. HERMENS. Succinylphenylhydrazide or 1-Phenyl- 3 : 6-orthopiperazine	i, 370
LIEBERMANN (C.) and A. BISTRZYCKI. Action of Ammonia and Hydr- azine on Opianic and Phthalaldehydic acids	i, 371
KÖTZ (A.). Derivatives of Dichloroquinazoline	i, 372
WOLLFF (L.). Pyrazine	i, 373
ABENIUS (P. W.). Paradiazine Derivatives	i, 374
BLADIN (J. A.). Oxidation of Azimidotoluene	i, 375
BLAU (F.). Constitution of Nicotine	i, 375
GOMBERG (M.). Trimethylxanthine Derivatives	i, 375
PRESCOTT (A. B.). Mercuriodides of Organic Bases	i, 376
KOENIGS (W.). Oxidation Products of Apocinchene	i, 376
EOINHORN (A.) and Y. TAHARA. Constitution of Anhydroecgonine	i, 377
SOLDIANI (A.). Alkaloids of the Seeds of <i>Lupinus albus</i>	i, 379
RAMSDEN. Proteids of White of Egg	i, 379
LORENZ (N. v.). Behaviour of Proteids to Concentrated Hydriodic acid	i, 379
OSBORNE (T. B.). Crystallised Vegetable Proteids	i, 380
WINTERSTEIN (E.). Tunicin	i, 380
SELIVANOFF (T.). Influence of Negative Groups in Organic Compounds	i, 381
KONDAKOFF (I.). Composition of Commercial Amylene	i, 381
KONDAKOFF (I.). Syntheses in the Fatty Series by means of Zinc Chloride	i, 382
BEVAD (I.). Ethereal Salts of Nitrous acid	i, 382
KONDAKOFF (I.). Action of Zinc Chloride on Fatty Alcohols	i, 382
KESSLER (A.). Action of Iodine on Sodium Propoxide	i, 383
KIJNER (N.). Action of Sodium on Epichlorhydrin	i, 383
SCHUNCK (E.) and L. MARCHLEWSKI. Phlorose	i, 384
ASBÓTH (A. v.). Action of Hydrogen Peroxide on Starch	i, 384
TANRET (C.). Inulin, Pseudoinulin, and Inulenin	i, 385
FRÄNKEL (S.). Glycogen	i, 386
NASTIUKOFF (A.). Witz's Oxycellulose	i, 387
VIGNON (L.). Absorption of Mercuric Chloride from Dilute Solutions by Cotton	i, 387
LE BEL. Dimorphism of Dimethylamine Platinochloride	i, 387
SELIVANOFF (T.). Haloïd Substitution Products of Amides	i, 388
THIELE (J.). Nitrosoguanidine	i, 389
PULVERMACHER (G.). Formaldehyde	i, 389
WIBLICENUS (W.), T. KIRCHSEISEN, and E. SATTLER. Condensation of Chloral with Ketones	i, 389
ZELINSKY (N.) and S. KRAPIVIN. Pinacone from Ethyl Methyl Ketone	i, 390
FAVORSKY (A. E.). Action of Potassium Carbonate on Dichloro ketones	i, 391
SIMONINI (A.). Action of Iodine on the Silver Salts of Fatty Acids	i, 391
RUBTZOFF (P. P.). Oximidoacetic acid	i, 391
SELIVANOFF (T.). Amides of Hypoiodous acid	i, 392
KURBATOFF (D.). Presence of Linoleic acid in some Animal Fats	i, 392
VIEFHAUS (A.). Propylideneacetic acid and Ethylidenepropionic acid	i, 392
HOLT (A.) and J. BARUCH. Action of Sulphuric acid on Behenic acid	i, 393
HAGEMANN (C. T. L.). Action of Methylene Iodide on Ethylic Aceto- acetate	i, 393

	PAGE
BROWN (A. CRUM) and J. WALKER. Electrolytic Synthesis of Bibasic Acids.	i, 394
GIGLI (T.). Decomposition of Solutions of Oxalic acid	i, 395
SEMMLER (F. W.). Derivatives of β -Methyladipic acid	i, 396
FLEISCHHAUER (H.). Condensation of Cyanides with Ethereal Salts by means of Sodium Ethoxide	i, 396
BRÜCK (P.). Di-iodides of Tetrolic and Acetylenedicarboxylic acids	i, 397
HENRY (P.) and H. v. PECHMANN. Action of Nitrous acid on Ethylic Acetonedicarboxylate.	i, 397
PECHMANN (H. v.) and F. NEGER. Action of Acetic Anhydride on Acetonedicarboxylic acid	i, 398
PECHMANN (H.) v. Coumalinic acid	i, 401
FEIST (F.). Formation of Coumalin Rings	i, 403
MIOLATI (A.). Thiocyanacetamide and Isothiohydantoin	i, 405
MATIGNON (C.). Hydrylic and Dehydroxymalic acids	i, 405
LIEBERMANN (C.). Thiophen of Crystallisation	i, 406
NOYES (A. A.) and A. A. CLEMENT. Electrolytic Reduction of Nitrobenzene dissolved in Sulphuric acid	i, 406
TÖHL (A.) and E. BAUCH. Di-iodometaxylenes obtained from Iodo-metaxylenes and Sulphuric acid	i, 407
TÖHL (A.) and R. ECKEL. Reactions of Iodimesitylene	i, 407
FOURNIER (H.). Paradiethylbenzene	i, 408
TÖHL (A.) and A. MÜLLER. Behaviour of Halogen Derivatives of ψ -Cumene towards Sulphuric acid.	i, 408
FOURNIER (H.). Pentethylbenzene	i, 409
DE FORCRAND. Compounds of Alkali Phenoxides with Phenol	i, 409
CIAMICIAN (G.) and P. SILBER. Symmetrical Dimethoxyquinone	i, 409
BERNTHSEN (A.). Metamidodialkylorthotoluidines	i, 409
HANTZSCH (A.). Compounds containing Double Linking between Nitrogen and Carbon	i, 409
WITT (O. N.) and F. MAYER. Azo-derivatives of Catechol	i, 410
ROTHENBURG (R. v.). Action of Hydrazine Hydrate on Organic Halogen Compounds	i, 410
WIDMAN (O.). New Method of preparing Unsymmetrical Derivatives of Phenylhydrazine	i, 411
HANTZSCH (A.). Hydrochlorides of Stereoisomeric Aldoximes	i, 411
LACHAUD (M.) and C. LEPIERRE. Oxidation and Sulphonation of Organic Compounds by Ammonium Hydrogen Sulphate	i, 411
MAZZARA (G.). Unsymmetrical Dibenzylthiocarbamide	i, 411
CAZENEUVE (P.). Gallanilide and its Triacetyl and Tribenzoyl Derivatives	i, 412
HERZIG (J.) and T. v. SMOLUCHOWSKI. Quercetin Derivatives	i, 413
DE CONINCK (O.). Isomeric Amidobenzoic acids	i, 413
FORTMANN (G.). Orthomethamidobenzoic acid	i, 414
LIEBERMANN (C.) and A. HARTMANN. Optically Active Cinnamic acid Dibromides.	i, 414
LIEBERMANN (C.) and H. FINKENBEINER. Optically Active Cinnamic acid Dichlorides	i, 415
BECK (C.). Orthonitrobenzyl Derivatives	i, 415
GABRIEL (S.) and A. NEUMANN. Conversion of Phthalide Derivatives into those of $\alpha\alpha$ -Diketohydrindone	i, 415
OTTO (R.) and J. TRÖGER. Diphenylsulphone and Ditolylsulphone Ethyl Ethers	i, 415
OTTO (R.). Anilides of Beuzenesulphonic and Paratoluenesulphonic acids	i, 416
OTTO (R.) and J. TRÖGER. Non-existence of Stenhouse's Phenylthio-sulphuric acid. Sulphonic acids of Phenyl Sulphide. Bunte's Salt	i, 416
CIAMICIAN (G.) and P. SILBER. Leucotin and Cotogenin	i, 417
BIZZARI (D.). Carbazacridines: Oxidation of Phenylcarbazacridine	i, 417
FERNAU (A.). Isocarhostyryl	i, 417
LIEBERMANN (C.) and H. SACHSE. Constitution of the Truxillic acids	i, 418

KNOEVENAGEL (E.). Formation of Cycloïd Compounds from 1 : 5-Diketones. Structural Isomeride of Camphor	i, 419
HALLER (A.) and A. GUYOT. Derivatives of Phenolphthaleïn and Fluoresceïn	i, 419
JUKOVSKY (S.). Octonaphthylene and Octonaphthenic Alcohol	i, 420
GAESS (F.) and E. ELSAESSER. Condensation of Metaphenylenediamine with α -Naphthol	i, 420
REVERDIN (F.) and C. DE LA HARPE. Preparation of Naphthidine	i, 421
LEROY (J. A.). Derivatives of α -Naphthylacetylene and of β -Methylacetylene	i, 421
LITTHAUER (S.). Substantive Cotton Dyes from Diamidophenanthraquinone	i, 422
TOLOTCHKO. Action of Sulphuric acid on Menthol	i, 422
ODDO (G.). Camphor	i, 422
BRÜHL (J. W.). Ethereal Salts of Camphoric acid	i, 423
THIEL (W.). Derivatives of Campholenic acid	i, 423
KROMER (N.). Glucosides of the Convolvulaceæ	i, 423
MASSON. Active Principles of Bryony Root	i, 424
KOBERT (R.). Saponins	i, 424
KLEIN (J.). Action of Phosphoric Chloride on Santonin	i, 425
KLEIN (J.). Derivatives of Santonin	i, 425
GRASSI-CRISTALDI (G.). Fumaroid and Maleinoid Structure of some of the Derivatives of the Santonins	i, 425
GRASSI-CRISTALDI (G.). Action of Hydrochloric acid on the Santonins Bisdihydrosantoninic acid	i, 425
HERZIG (J.). Methylbrazilin	i, 426
BAMBERGER (E.). Constitution of Five-membered Rings	i, 426
LADENBURG (A.). Synthesis of Oxypyridine and Oxypiperidine Bases	i, 426
LADENBURG (A.). Resolution of β -Pipicoline into its Optical Isomerides	i, 427
PINKUS (G.). Penthiazolines	i, 427
FISCHER (E.). Formation of Isoquinoline	i, 427
GARZINO (L.). Triphenylpiperazine	i, 428
ROTHENBURG (R. v.). Pyrazolone	i, 428
BUCHNER (E.). Synthesis of Pyrazole Derivatives by means of Ethylic Diazoacetate	i, 429
BUCHNER (E.) and A. PAPENDIECK. Pyrazoline-3 : 5-dicarboxylic acid	i, 430
BUCHNER (E.) and H. WITTER. Pyrazolone-3 : 4 : 5-tricarboxylic acid	i, 431
BUCHNER (E.) and A. PAPENDIECK. Pyrazole-3 : 5-dicarboxylic acid	i, 431
BUCHNER (E.) and M. FRITSCH. Pyrazole-3 : 4 : 5-tricarboxylic acid	i, 432
BUCHNER (E.) and M. FRITSCH. Preparation and Derivatives of Pyrazole	i, 432
BAMBERGER (E.). Imidazoles	i, 432
BAMBERGER (E.) and J. LORENZEN. Constitution and Formation of Benzimidazoles	i, 433
BAMBERGER (E.) and E. BERLÉ. Behaviour of the 2'-Methyl Group in Benzimidazoles	i, 435
BAMBERGER (E.) and B. BERLÉ. Opening of the Benzimidazole Ring	i, 437
BAMBERGER (E.) and B. BERLÉ. Addition of Chloral to Quinoline Bases and Benzimidazoles	i, 438
WOHL (A.) and W. MARCKWALD. Formula of Glyoxaline	i, 438
WIDMAN (O.). Formation of Dihydroquinazolines	i, 438
THIELE (J.) and J. T. MARAIS. Tetrazole Derivatives from Diazo-tetrazotic Acid	i, 440
JACOBI (F.) and C. STOEHR. A Homologue of Coniine	i, 442
LADENBURG (A.). Isoconiine and the Asymmetrical Nitrogen Atom	i, 442
PINNER (A.). Nicotine	i, 443
NASINI (R.) and A. PEZZOLATO. Decomposition of Salts of Nicotine and the Action of Alcohol on them	i, 444
EINHORN (A.) and F. K. DE NORWALL. Amides of Ecgonine	i, 445

	PAGE
LIEBERMANN (C.) and O. KÜHLING. Hygrineoxime	i, 446
BIRSMANN (E.). Alkaloids of <i>Corydalis nobilis</i>	i, 446
FREUND (M.) and C. FAUVET. Geissospermine	i, 446
PLANTA (A. v.) and E. SCHULZE. Stachydrine	i, 447
HERZ (F. J.). Amyloid, a Component of Milk: Dairy Products	i, 447
BERTIN-SANS (H.) and J. MOITESSIER. Oxyhæmatin, Reduced Hæmatin, and Hæmochromogen	i, 447
BERTIN-SANS (H.) and J. MOITESSIER. Action of Carbonic Oxide on Reduced Hæmatin and Hæmochromogen	i, 448
MAQUENNE (L.). Preparation of Tetraiodoethylene	i, 449
HERZFELDER (A. D.). Substitution in the Fatty Series	i, 449
NERNST (W.) and C. HOHMANN. Formation of Amylic Salts from Acids and Amylene	i, 449
KUTCHEROFF (M. G.). Action of Mercury Salts on Unsaturated Hydrocarbons and Alcohols	i, 450
GRINER (G.). Synthesis of Erythritol	i, 450
BOURQUELOT (E.). Trehalase, a Ferment for Trehalose	i, 451
PETIT (P.). Calcium Sucrates	i, 451
SCHLÖMANN (W.). Action of Metaphosphoric acid on Organic Bases	i, 452
DEMYANOFF (N.). Action of Nitrous acid on Tetramethylenediamines	i, 453
COMBES (A.) and C. COMBES. Action of Ammonia and of Aliphatic Amines on Acetylacetone	i, 454
COMBES (A.) and C. COMBES. Action of Diamines on Acetylacetone	i, 454
FARMAKOVSKY (N.). Tar from the Bark of <i>Populus tremula</i>	i, 454
FIQUET (E.). Condensation of Aliphatic Aldehydes with Cyanacetic acid	i, 455
WISLICENUS (J.). Brom-additive Products of Angelic and Tiglic acids	i, 455
JUILLARD (P.). Turkey Red Oil	i, 455
HELD (A.). Condensation of Alkyl Acetocyanacetates	i, 456
ROSENHEIM (A.). Oxalic acid Derivatives	i, 457
COLSON (A.). Stereochemistry of Malic Derivatives: Variations in the Rotatory Power of Liquids	i, 457
SELIVANOFF (T.). Trichloromethanesulphonic Chloride	i, 458
BAUMANN (E.) and G. WALTER. Hydrolysis of Sulphones, Sulphone-sulphinic acids, and Sulphinolactones	i, 458
KIJNER (N.). Hydrogenisation of Benzene	i, 460
PICTET (R.). Formation of Nitro-derivatives at Low Temperatures	i, 460
TASSINARI (G.). Constitution of the Dihydroxythiobenzenes	i, 461
PECHMANN (H. v.). Bülow's Reaction and the Oxidation of Hydrazones	i, 461
SCHALL (C.). Wessel's Dicarbo-base from Phenylhydrazine and Carbo-diphenylimide	i, 461
CURTIS (T.). Hippurylphenylbuzylene: New Synthesis of Azoimide	i, 463
BECKMANN (E.) and A. KÖSTER. Basic Bye-product obtained by benzylating Acetoxime	i, 464
MEYER (L.). Spectroscopical Investigation of Salts of Aromatic Bases	i, 464
FISCHER (O.) and E. HEPP. Constitution of the Mauveïnes	i, 464
CLAISEN (L.) and O. MANASSE. Action of Chlorine on Isonitrosoketones	i, 464
CLAUS (A.). Aromatic Alkyl Ketones	i, 464
DE CONINCK (O.). Isomeric Amidobenzoic acids	i, 465
HALLER (A.) and E. BRANCOVICI. Alkyl Benzeneazocyanacetates	i, 465
THORP (F. H.). Action of Hydroxylamine on Orthobenzoylebenzoic acid	i, 466
FILETI (M.) and G. BALDRACCO. Homoterephthalic acid	i, 467
MULLER (P. T.). Ethylic Phthalocyanacetate	i, 467
BAMBERGER (E.) and E. A. ZUMBRO. Dihydromethylketole	i, 468
MEYER (V.), O. LIST, J. MARCUSSEN, and W. A. BONE. Indoxazen Derivatives	i, 469
TEICHMANN (H.). Preparation of Benzidine Sulphate	i, 469
ERDMANN (E.). Preparation of Benzidine	i, 470
MÖHLAU (R.) and E. FRITZSCHE. Formation of Acridine Dyes	i, 470
MEYER (R.) and E. SAUL. Xanthydrol	i, 471

	PAGE
HOFMANN (K.). Colouring Matters of the Triphenylmethane Series . . .	i, 472
STOCK (A.). Auramines . . .	i, 472
MEYER (R.) and E. SAUL. Action of Phenylhydrazine on Lactones . . .	i, 473
BECKMANN (E.) and A. KÖSTER. Hydroximido-derivatives. Benzile-oximes . . .	i, 474
SCHMID (J.). Constitution of β -Hydroxynaphthoic acid (m. p. 216°) . . .	i, 475
SCHÖPFF (M.). Constitution of β -Hydroxynaphthoic acid (m. p. 216°) . . .	i, 476
HIRSCH (R.). α -Hydroxynaphthoic acid (m. p. 216°) . . .	i, 476
JAUBERT (G. F.). 1:1'-Naphthalic acid and its Derivatives . . .	i, 477
REVERDIN (F.) and C. DE LA HARPE. Amidonaphtholsulphonic acids . . .	i, 478
GEORGESCU (M.). Benzenesulphonates of the Aromatic Series . . .	i, 478
CLAISEN (L.) and O. MANASSE. Isonitrosocamphor and its Derivatives . . .	i, 479
MERCK (E.). Champacol, a New Camphor . . .	i, 480
CLAISEN (L.). Hydroxymethylene Compounds . . .	i, 480
LÜDY (F.). Gum Benzoïn from Sumatra . . .	i, 480
SCHMIDT (E.). Constituents of Sumatra Gum Benzoïn . . .	i, 481
MERCK (E.). Adonite . . .	i, 481
PLUGGE (P. C.). Cerberin . . .	i, 481
KROMER (N.). Glucoside of <i>Ipomœa pandurata</i> (<i>Convolvulus panduratus</i> , L.) . . .	i, 482
ANDERLINI (F.). Derivatives of Cantharidin . . .	i, 483
ANDERLINI (F.). Action of Diamines on Cantharidin . . .	i, 483
GUARESCHI (J.). Synthesis of Hydropyridine Compounds . . .	i, 484
CLAUS (A.) and E. PYCHLAU. 4'-Bromonicotinic acid . . .	i, 484
CLAUS (A.) and H. HOWITZ. Hydroxyquinolines . . .	i, 484
STOEHR (C.). Pyrazines and Piperazines . . .	i, 486
BLAU (F.). Constitution of Nicotine . . .	i, 489
SCHMIDT (E.). Salts of Caffeine . . .	i, 489
CLAUS (A.). Papaverine Ethobromides . . .	i, 489
SCHMIDT (E.), G. KOENIG, and W. TIETZ. Alkaloids of the Papaveraceæ . . .	i, 490
MERCK (E.). Crystallised Veratrine . . .	i, 490
MERCK (E.). Relation between Atropine, Apotropine, and Belladonnine . . .	i, 491
MERCK (E.). Hyoscyamine . . .	i, 491
MERCK (E.). Pseudohyoscyamine . . .	i, 491
MERCK (E.). Hydrastine Hydrogen Tartrate . . .	i, 491
MERCK (E.). Alkaloids from <i>Corydalis cava</i> . . .	i, 492
SPIEGEL (L.). Gelseminine . . .	i, 492
ENGLER (C.) and L. SINGER. Recognition of Paraffin and of Lubricating Oil in the Distillate of Train Oil under pressure . . .	i, 493
BARBIER (P.). Licarene from Licareol . . .	i, 493
BAMBERGER (E.) and L. SEEBERGER. Constitution of Dicyanodiamide . . .	i, 494
HOLLEMANN (A. F.). Structure of Fulminates: Dibromonitracetonitrile . . .	i, 494
KRÜGER (T. R.). Ethereal Hydrogen Sulphates from Secondary Alcohols . . .	i, 495
BARBIER (P.). Derivatives of Licareol . . .	i, 495
BARBIER (P.). Constitution of Licareol . . .	i, 496
SCHEIBLER (C.) and H. MITTELMEIER. Trehalose, a New Carbohydrate . . .	i, 496
BOURQUELOT (E.). Inulase and the Indirect Alcoholic Fermentation of Inulin . . .	i, 497
WINTERSTEIN (E.). Tunicin . . .	i, 497
BERG (A.). Chloramines . . .	i, 497
SCHEIBLER (C.). Action of Alkalis on Betaine . . .	i, 498
ORNDORFF (W. R.) and S. W. Young. Condensation Products of Acetone with Concentrated Sulphuric acid . . .	i, 498
TRAPKONZJANZ (C.). Ketoximes . . .	i, 499
ENGLER (C.) and M. STEUDE. Behaviour of Trichloroacetic acid at a High Temperature . . .	i, 499
BISCHOFF (C. A.) and P. WALDEN. Application of the Dynamical Hypothesis to Keto-acid Derivatives . . .	i, 499
WALKER (J.). Action of Alcohols on Lactones and Alkyl Salts . . .	i, 500

	PAGE
GUYE (P. A.). Malic acid Derivatives	i, 500
GMELIN (B.). Constitution of Leucine	i, 501
WERNER (A.). Hydroxylamineacetic acid.	i, 501
MILLER (W. v.) and J. PLÖCHL. Amidoxylic acids.	i, 502
MICHAELIS (A.). Thionylamines	i, 504
MICHAELIS (A.) and O. STORBECK. Thionylamines of the Aromatic Series	i, 504
GENVRESSE (P.). Syntheses with Aluminium Chloride	i, 505
WILLGERODT (C.). Iodoso- and Iodoxy-compounds.	i, 505
WILLGERODT (C.). Orthochloriodoso- and Orthochloriodoxy-benzene	i, 506
ASKENASY (P.) and V. MEYER. Iodoso-compounds	i, 506
PERRIER (G.). Metallic Compounds of the Benzene Series	i, 508
PINNOW (J.) and G. PISTOR. Action of Formaldehyde on Nitrosodimethylaniline	i, 509
WOHL (A.). Action of Phenylhydrazine on Diazobenzene	i, 509
KRÜCKEBERG (F.). Ethylic Azobenzenecyanacetate	i, 509
WERNER (A.). Stereoisomerism of the Benzhydroxamic acids	i, 510
CAZENEUVE (P.). Constitution of Gallic Blue and Tannin Indigo	i, 510
LIEBERMANN (C.). Theory of the Formation of Coloured Compounds with Mordants	i, 510
BISCHOFF (C. A.) and P. WALDEN. Anilides and Toluidides which exist in two Modifications	i, 511
ENGLER (C.) and L. DENGLE. Condensation of Acetophenone on heating alone or with Zinc Chloride	i, 512
ENGLER (C.) and E. LÖW. Behaviour of Organic Acids and Ethereal Salts at High Temperatures	i, 512
LIEBERMANN (C.). New Synthesis of Allocinnamic Acid.	i, 513
KARSTEN (W.). Condensation of Cinnamic acid with Hydrocarbons	i, 513
ECKENROTH (H.) and M. WOLF. Phenylic and α - and β -Naphthyllic Salicylates	i, 514
ROUFFAER (H. A.). Action of Phthalic Chloride on Trinitraniline	i, 515
MICHAELIS (A.) and O. STORBECK. Action of Thionyl Chloride on Benzylamine.	i, 515
MICHAELIS and others. Thionylamines of the Aromatic Series	i, 515
SPILKER (A.). Indene and Hydrindene	i, 518
BISCHLER (A.) and P. FIREMAN 2': 3'-Diphenylindoles	i, 519
BAMBERGER (E.) and H. STERNITZKI. Dihydromethylketole	i, 520
EPHRAIM (J.). Action of Phenylhydrazine on Lactones	i, 522
MÖHLAU (R.) and R. BERGER. Phenyl-naphthalenes and Zincke's Hydrocarbon $C_{12}H_{16}$	i, 522
BERTRAND (G.). Essential Oil of Niaouli	i, 523
BOUVEAULT (L.). Liquid Isomeride of Hydrocamphene	i, 523
ÉTARD (A.). Action of Zinc Chloride on Chlorocamphor: Relation between Camphor and Carvacrol	i, 524
RUPE (H.) and C. MAULL. Camphoric acid Derivatives	i, 524
AUWERS (K.) and H. SCHNELL. Camphoric acid	i, 525
MINGUIN (J.). Bromal Borneolates	i, 526
ANDREOCCHI (A.). New Isomeride of Santonin and Santonous acid	i, 526
RUHEMANN (S.). Dihydroxypyridines	i, 527
EINHORN (A.) and A. W. GILBODY. Action of Chloral on Pyridine Bases from Messel	i, 527
BAMBERGER (E.) and W. DIECKMANN. Tetrahydroisoquinoline	i, 528
BISCHLER (A.) and E. BURKART. Phenometadiazine Derivatives	i, 530
BISCHLER (A.) and F. J. HOWELL. Phenometadiazine Derivatives	i, 531
SALOMON (A.). Oxazolines and Thiazolines	i, 532
FREUND (M.) and H. HAASE. Paranitrophenylmethoxybiazalone and its Decomposition Products	i, 534
BALKE (P.). Xanthine Derivatives	i, 535
VIS (G. N.). Constitution of Morphine	i, 536
EYKMAN (J. F.). Formula of Tropine	i, 537

	PAGE
EINHORN (A.) and A. FRIEDLÄNDER. nor- γ -Ecgonine	i, 537
GARCIA (A.). Ptomaines	i, 538
EICKHOLZ (A.). Urobilin	i, 538
ROBIN (H.). Urinary Colouring Matters	i, 539
PETIT (P.). Vegetable Nuclein	i, 539
HUGOUNENQ (L.). Filtration of Casein Solutions through Porcelain	i, 540
KONDAKOFF (I.). Action of Mineral Acids on Dimethylallene	i, 541
ZETTEL (T.). Cyanogen	i, 541
BOUVEAULT (L.). Hydrolysis of Aromatic Nitriles	i, 541
WILM (T.). Sodium Platinocyanide	i, 541
SCHOLL (R.). Fulminic acid and its Derivatives	i, 542
TISSIER (L.). Normal Amyl Alcohol	i, 542
TISSIER (L.). Fourth Primary Amyl Alcohol	i, 542
SAYTZEFF (N.). Allylmethylethylcarbinol	i, 544
BOYANUS (A.). Allylmethylhexylcarbinol	i, 544
BOUCHARDAT (G.). Action of Acetic Anhydride on Linalol	i, 544
BARBIER (C.). Licarhodol from Licareol	i, 544
PANFILOFF (I.). Ethylmethylpropylethylene Glycol	i, 545
TOLLENS (B.). Birotation of Glucose	i, 545
KILIANI (H.) and H. SANDA. Decomposition of Galactose by Calcium Hydroxide	i, 546
BÉCHAMP (A.). Absence of Spontaneous Inversion of Cane Sugar in Aqueous Solution at the ordinary Temperature	i, 547
STONE (W. E.). Recent Investigations on Carbohydrates	i, 547
FRIEDEL (C.). Metaldehyde	i, 547
HERSCHMANN (P.). Action of Sulphuric acid on the Pinacone of Methyl Ethyl Ketone	i, 547
DESZÁTHY (A.). Solubility of Barium and Calcium Butyrates	i, 547
LIDOFF (A.). Solubility of the Lead Salts of Stearic and Palmitic acids in Ether	i, 548
TALANTZEFF (Z.). Behenic acid	i, 548
GASCARD (A.). Wax of Gum Lac	i, 548
MOUREU (C.). New Method of preparing Acrylic acid	i, 548
KONDAKOFF (I.). Oxidation of β -Chlorocrotonic acid	i, 549
SAYTZEFF (M. C.) and A. SAYTZEFF. Action of Sodium Hydrogen Sulphite and of Sulphuric acid on Oleic and Erucic acids	i, 549
ALEXANDROFF (P.) and N. SAYTZEFF. Isoerucic acid	i, 549
LEBEDEFF (I.). Transformation of Elaïdic acid into Oleic and Isoleic acids	i, 550
SAYTZEFF (N.). Transformation of Brassidic acid into Erucic and Isoerucic acids	i, 550
JUKOVSKY (M.). Oxidation of Brassidic acid	i, 550
SAYTZEFF (A.). Structure of Oleic, Erucic, and Isomeric acids	i, 551
FILETI (M.). Oxidation and Derivatives of Erucic acid	i, 551
BARUCH (J.). Constitution of Behenolic acid	i, 551
SIMON (L.). Derivatives of Pyruvic acid	i, 552
GENYRESSE (P.). Ethylic Pyruvate and the Product of its Condensation by Hydrogen Chloride	i, 552
KEHRMANN (F.) and N. PICKERSGILL. Some New Complex Oxalates	i, 552
BRUNNER (K.). Dimolecular Propionic Cyanide. Ethyltartronic acid	i, 553
COLSON (A.). Formula of ordinary Tartaric acid	i, 553
MICHAELIS (A.) and H. SIEBERT. Action of Thionyl Chloride on Acid Amides	i, 553
CHANCEL (F.). Dipropylamidoacetic acid	i, 554
CHANCEL (F.). Tripropylamidoacetic acid	i, 554
DRCEV (T.). Oxalyl Derivatives	i, 554
KEP (W.). Action of Ammonia on Mesiten Lactone and its Derivatives	i, 554
HENTZSCHEL (W.) and J. WISLICENUS. Adipin Ketone	i, 555
HENTZSCHEL (W.). Adipin Ketone from Wood Oil	i, 556

	PAGE
HENTZSCHEL (W.) and J. WISLICENUS. Pentamethylenic Alcohol and its Derivatives	i, 556
GÄRTNER (C.). Pentamethylene and its Derivatives	i, 557
GÄRTNER (C.). Pentamethylenecarboxylic acid	i, 557
MAGER (H.). Constitution of Suberone and of the Closed-chain Ketones of Pimelic and Azelaic acids	i, 557
LOOPT (E.). Constituents of Wood Oil	i, 558
ZINCKE (T.) and O. FUCHS. Imido-derivatives of Chlorinated Diketo-pentene	i, 558
VAUBEL (W.). Action of Nascent Bromine on some Benzene Derivatives	i, 560
WILLGERODT (C.). Iodoso- and Iodoxy-compounds	i, 561
SCHRAMM (J.). Action of Aluminium Chloride on Chlorides and Bromides of Aromatic Radicles	i, 561
GENVRESSE (P.). Some Substituted Benzenoid Hydrocarbons.	i, 562
SCHRAMM (J.). Cinnamene Hydrochloride and Hydrobromide.	i, 563
FISCHER (B.) and B. GRÜTZNER. Homologues of Phenol	i, 563
DE CHAMBRIER (P.). Supposed Formation of Orthocresol from Methylsalicylic acid	i, 563
JACKSON (C. L.) and H. S. GRINDLEY. Hemiacetals derived from Substituted Chloranils	i, 563
EHRlich (P.) and G. COHN. Action of Acid Chlorides on Nitrosodimethylaniline	i, 564
REISSERT (A.). Products of the Action of Aniline on Dibromosuccinic acid	i, 564
JUNGHahn (A.) and A. REISSERT. Action of Paratoluidine on Dibromosuccinic acid. New Derivatives of Dianilidosuccinic acid	i, 565
GATTERMANN (L.). Electrolytic Reduction of Aromatic Nitro-compounds	i, 566
LUMIÈRE (A.) and A. SEYEWITZ. Action of Sodium Sulphite on Salts of Amidophenols	i, 568
POSNER (T.). Cinnamylamine and its Derivatives	i, 568
ANGELI (A.). Action of Nitrous acid on Ketoamines	i, 570
MICHAEL (A.). Action of Diazobenzeneimide on Methylacetylenedicarboxylate	i, 570
TÄUBER (E.). Nitrohydroxyazo- and Nitroamidoazo-compounds	i, 570
WITT (O. N.) and E. S. JOHNSON. Azo-derivatives of Quinol	i, 571
HARRIES (C. D.). Action of Ethylenic Bromide on Phenylhydrazine	i, 571
BOUVEAULT (L.). So-called Hydrazine of Cyanacetone	i, 571
LOSSEN (W.). Stereoisomerism of the Benzhydroxamic acids	i, 572
LINDNER (R.). The two Isomeric Benzyl Derivatives of Nitroso- β -benzylhydroxylamine	i, 572
MIOLATI (A.). Paramagenta	i, 572
TRILLAT (A.). New Series of Colouring Matters	i, 573
FINGER (H.). Derivatives of Orthamidobenzamide	i, 574
HANTZSCH (A.) and A. MIOLATI. Anhydri-sation of Oximido-acids.	i, 574
FROMM (E.). Phenylldithiobiuret	i, 575
BILLETER (O.). Penta-substituted Dithiobiurets	i, 575
CLAISEN (L.). Benzoyl Derivatives of Benzoylacetone	i, 577
WACHTER (W.). Orthiodobenzoic acid and its Derivatives	i, 577
HARTMANN (C.) and V. MEYER. Iodoxybenzoic and Iodosobenzoic acids	i, 577
ALLEN (L. S.). Iodoso- and Iodoxy-derivatives of Metanitropariodobenzoic acid	i, 578
PERRIER (G.). Metallic Compounds of the Benzene Series	i, 578
ORNDORFF (W. R.) and J. WHITE. Molecular Weight of Hydrogen Peroxide and of Benzoyl Peroxide	i, 579
WEISS (F.). Phenylc Hippurate and its Condensation Products	i, 579
ERLENMEYER (E., Jun.). Condensation of Hippuric acid with Phthalic Anhydride and with Benzaldehyde	i, 580

	PAGE
CLAUS (A.) and E. STAPELBERG. Parachlororthotoluic acid and its Derivatives	i, 580
KLOEPPPEL (E.). Iodoxy- and Iodoso-derivatives of Paratoluic acid	i, 581
ERLENMEYER (E., Jun.). α -Benzoylamidophenylpropionic acid	i, 581
ERLENMEYER (E., Jun.). Separation of Cinnamic acid Dibromide into its Optically Active Constituents	i, 582
LIEBERMANN (C.). Optically Active Cinnamic acid Dibromides	i, 582
LIEBERMANN (C.) and A. HARTMANN. Optically Active Cinnamic acid Dibromides	i, 582
ERLENMEYER (E., Jun.). Benzoylamidocinnamic acid	i, 582
MACH (H.). Abietic acid	i, 582
HANTZSCH (A.) and A. MIOLATI. Formation of Inner Anhydrides from Ketoximic acids	i, 583
LIEBERMANN (C.). Addition of Sodium Alkylloxides	i, 583
BIÉTRIX (A.). Bromogallic acid and its Derivatives	i, 583
SCHMIDT (R.). Alkyltoluidinesulphonic acids	i, 584
METCALF (W. V.). Action of Alcohols on Paradiazotoluenemetasulphonic acid	i, 585
PARKS (R. M.). Action of Methyl Alcohol on Paradiazotolueneorthosulphonic acid	i, 585
CLAUS (A.) and R. BAYER. Monochloro-derivatives of Orthoxylene, and their Relation to the Chlororthotoluic acids	i, 586
KÖNIG (A.). α -Hydrindone and its Derivatives	i, 586
BENEDIKT (H.). β -Hydrindone and its Derivatives	i, 587
MEYENBURG (F. v.). Synthesis of α -Phenylindoxazen	i, 587
TÄUBER (E.). Orthodiamidodiphenyls	i, 588
LÖWY (R.). Tetramethoxydiphthalyl	i, 588
BOUVEAULT (L.). Preparation of Triphenylacetoneitrile and Triphenylcarbinol	i, 589
THORP (F. H.). Action of Hydroxylamine on Orthobenzoylbenzoic acid	i, 589
KLINGEMANN (F.). Condensation of Deoxybenzoïn with Aldehydes and Ketones	i, 589
KLINGEMANN (F.). Diphenylacetic acid	i, 590
BAMBERGER (E.) and W. LODTER. Dihydronaphthalene and its Derivatives	i, 591
GRAEBE (C.) and F. BOSSEL. Oxidation of Naphthalic acid	i, 593
BAMBERGER (E.) and F. CHATTAWAY. Chrysene	i, 593
BAMBERGER (E.) and F. CHATTAWAY. Picene	i, 594
LONG (J. H.). American Oil of Turpentine	i, 594
WALLACH (O.), and F. KERKHOFF. Terpeneol	i, 595
WALLACH (O.), H. KRUSE, and F. KERKHOFF. Dihydrocarveol	i, 595
WALLACH (O.). Oxidation of Terpene Derivatives	i, 596
CAZENEUVE (P.). Constitution of Camphor	i, 598
ASCHAN (O.). Bromocamphoric Anhydride and Camphoric acid	i, 598
HOOGWERFF (S.) and W. A. VAN DORP. Ethyl Hydrogen Camphorate	i, 599
HOOGWERFF (S.) and W. A. VAN DORP. Substituted Iso-imides of Camphoric acid	i, 599
FRIEDEL (C.) and A. COMBES. Action of Phenylhydrazine on Camphoric Anhydride and Etheral Camphorates	i, 600
DIETERICH (E.). Preparation of Cantharidin	i, 600
GOLDSCHMIEDT (G.) and F. v. HEMMELMAYR. Scoparin	i, 601
GINTL (W. H.). Urson	i, 601
KLINGEMANN (F.). New Nitrogenous organic acid	i, 602
CIAMICIAN (G.) and C. U. ZANETTI. Basic Properties of Pyrroline Derivatives	i, 602
STOEHR (C.). Piperidine Bases of the β -Series	i, 602
FERRATINI (A.). Conversion of Indoles into Quinolines	i, 602
MARCKWALD (W.) and others. Constitution of Cycloid Systems	i, 603
ROSENHEIM (O.) and J. TAFEL. Oxidation of Parahydroxyquinoline	i, 603

VIS (G. N.). Isomerides and Congeners of "Analgen," Ethoxy-4-benzoyl-amidoquinoline	i, 606
POMERANZ (C.). New Synthesis of Isoquinoline	i, 607
BISCHLER (A.) and B. NAPIERALSKI. New Synthesis of Isoquinoline	i, 608
FORTNER (P.). Isoquinoline Derivatives	i, 608
BISCHLER (A.) and W. OSER. Phenylmetadiazine Derivatives	i, 609
BISCHLER (A.) and W. OSER. New Synthesis of Pyrazole Derivatives	i, 610
ROTHENBURG (R. v.). Pyrazolone from Ethylic Acetylenedicarboxylate.	i, 611
ROTHENBURG (R. v.). Pyrazolone from Ethylic Propiolate	i, 611
MICHAELIS (A.) and O. LAMPE. Phenylpyrazolidine	i, 611
STOEHR (C.). Pyrazines	i, 612
WOLFF (L.). Synthesis of Pyrazine	i, 612
STOEHR (C.) and M. WAGNER. Methylpyridyls	i, 612
FISCHER (O.) and E. HEPP. Relation of Safranines to Indulines	i, 613
CUSHNY (A. R.). Alkaloids of <i>Gelsemium sempervirens</i>	i, 614
GRIFFITHS (A. B.). Ptomaine from the Urine in Cases of Eczema	i, 614
KRAWKOW (N. P.). Chitins	i, 615
GRIFFITHS (A. B.). δ -Achroglobin from the Blood of certain Mollusca	i, 615
PICKERING (J. W.). Proteid Reactions	i, 615
INOKO (Y.). Hæmoglobin which contains Phosphorus	i, 616
HÜFNER (G.). Dissociation of Oxyhæmoglobin in Aqueous Solution	i, 616
BURLS (F. B.), R. E. EVANS, and C. H. DESCH. Formation of Hydrocyanic acid by the Action of Nitric acid on Sugar, &c.	i, 617
HOSAEUS (H.). Pentaglycerol	i, 617
RAVE (P.) and B. TOLLENS. Penterythritol	i, 617
TANRET (C.). Carbohydrates of the Jerusalem Artichoke	i, 617
MAQUENNE. Lime Tree Honey.	i, 618
KISTYAKOVSKY (V.). Preparation of Glycogen from the Liver and Muscles	i, 618
HUPPERT. Specific Rotatory Power of Glycogen	i, 619
SABANÉEFF (A.) and I. ANTUSHEVITCH. Cryoscopy of Caramel	i, 619
LIPPETT (W.). Decomposition of Ethers by Hydrogen Haloids	i, 620
RAGOZIN (V.). Zinc Isopropide	i, 622
FLECK (H.). Alkyl Compounds of Magnesium	i, 622
MAGNANINI (G.). Action of Acetylacetone on Bromacetone in presence of Sodium Ethoxide	i, 623
HESSE (O.). Flowers of <i>Tagetes glandulifera</i>	i, 623
TANATAR (S.). Thermochemistry of Chloracetic acid	i, 624
KASTLE (J. H.) and B. C. KEISER. Decomposition of Chloracetates and Bromacetates	i, 624
TANATAR (S.). Thermochemistry of β -Dibromopropionic acid	i, 625
EHRENBERG (A.). Ethereal Oil from the Root of <i>Aspidium filix mas</i>	i, 625
PÉCHARD (E.). Combination of Oxalic acid with Titanic and Stannic acids	i, 625
ROSENHEIM (A.). Action of Inorganic Acid Metallic Oxides on Organic Acids	i, 626
SIMON (L.). Preparation of Amylic Pyruvate	i, 627
HOSAEUS (H.). Lactone from Formaldehyde and Pyruvic acid	i, 628
RAVE (P.) and B. TOLLENS. Lactone from Formaldehyde and Levulinic acid	i, 628
MAUMENÉ (E.). Preparation of Mucic acid from Gum Arabic	i, 628
NEF (J. U.). Ethylic Acetoacetate	i, 628
MULLIKEN (S. P.). Organic Electrosyntheses	i, 630
LENGFELD (F.) and J. STIEGLITZ. Nitrogen Halogen Compounds	i, 631
THOMAS-MAMERT (R.). Amidomaleamide and Oxysuccinamide	i, 632
SANI (G.). Essential Oil of <i>Cochlearia armoracia</i>	i, 633
CARRARA (G.). Isomeric Thetines	i, 633
MIOLATI (A.). Synthesis of Mercaptothiazoles	i, 634
BROCHET (A.) and P. LE BOULENGER. Condensation of Aliphatic Alcohols with Aromatic Hydrocarbons	i, 634

	PAGE
TRAPP (J.). Ethereal Oil of the Seeds of <i>Cicuta virosa</i>	i, 634
BROCHET (A.). Condensation of Hydrocarbons of the Benzene Series with those of the Ethylene Series	i, 635
MAQUENNE (L.). Identity of the Hydrocarbon C_7H_{14} derived from Perseitol and from Resin Oil with Heptanaphthene	i, 635
RUDEVITSCH (W.). A Decanaphthene from Caucasian Petroleum	i, 635
POTILITZIN (A. L.). Structure of Nitro-compounds and of the Oxides of Nitrogen	i, 636
JEDLICKA (K.). Derivatives of Paratertiarybutylphenol	i, 636
COUSIN (H.). Action of Sulphuric acid on Catechol and on Homo- catechol	i, 637
GUCCI (P.). Derivatives of Phenylenediamine	i, 638
CAZENÈVE (P.). Metallic Derivatives of Gallanilide	i, 638
ORNDORFF (W. R.) and C. G. HOPKINS. Decomposition of Diazobenzene Sulphate in Isoamyl Alcohol	i, 639
SHOBER (W. B.). Reaction of Alcohols with Paradiazobenzenesulphonic acid	i, 639
ALVISI (U.). Action of Phenylhydrazine on Ethylene Chlorhydrin	i, 639
PRUD'HOMME and C. RABAUT. Constitution of Colouring Matters of the Rosaniline Group	i, 640
ELBS (K.). Nitroquinol	i, 640
BUNGE (N. A.). Electrolysis of Substituted Organic Acids	i, 640
GRAEBE (C.). Preparation of Orthochloro- and Orthobromo-benzoic acids	i, 641
DE KONINCK (O.). Distinction between Isomeric Amidobenzoic acids and other Isomeric Compounds of the Benzene Series	i, 641
LAJOUX (H.) and A. GRANDVAL. Mercuric Salicylates	i, 642
DENOZZA (M.). Isoeugenolglycollic acid and Eugenolglycollic acid	i, 643
BIÉTRIX (A.). Triacetyldibromogallic acid and Tribenzoyldibromogallic acid	i, 643
CAUSSE (H.). Basic Gallate of Bismuth (Dermatol)	i, 643
GUCCI (P.). Action of Caustic Alkalis on Phthalides	i, 644
CERKEZ (S. G.). Rotatory Power of Salts of Quinic acid	i, 644
BIGINELLI (P.). Aldureides of Ethylic Acetoacetate and Ethylic Oxal- acetate	i, 645
D'ALADERN (R.). Heat of Formation of some Derivatives of Indigotin	i, 649
GRAEBE (C.) and K. LAGODZINSKI. Acridone	i, 649
ERDMANN (H.). Dichloronaphthalene	i, 651
ERDMANN (H.). Separation and Constitution of Isomeric Naphthalene Derivatives	i, 651
ERDMANN (H.) and C. SÜVERN. Isomeric α -Mononitronaphthalenemono- sulphonic acids	i, 651
ERDMANN (H.) and C. SÜVERN. Perinitronaphthalenesulphinic acid	i, 652
ERDMANN (H.) and F. HENKE. Derivatives of 3' : 1-Acetonaphthol	i, 652
ERDMANN (H.) and C. SÜVERN. Compounds of Substituted Naphthalene- sulphonic acids with Organic Bases	i, 653
ERDMANN (H.) and E. SCHWECHTEN. Synthetical Tri-derivatives of Naphthalene	i, 653
ERDMANN (H.). Sulphonation of α -Naphthylamine	i, 653
ERDMANN (H.). Synopsis of the Naphthylaminesulphonic acids	i, 655
ERDMANN (H.). Behaviour of Sodium or Potassium Naphthionate at High Temperatures	i, 655
ODDO (G.) and G. AMPOLA. Mixed Naphthylazo-compounds	i, 655
GRAEBE (C.) and E. GFELLER. Oxygenated Derivatives of Acenaphthene	i, 656
GRAEBE (C.) and C. A. WANDER. Phenanthridone	i, 658
PRUD'HOMME and C. RABAUT. Dihydroxyanthraquinoneformamides	i, 659
BERTRAM (J.) and H. WALBAUM. Pine Needle Oils	i, 659
ODDO (G.). Isonitrosocamphor	i, 660
ALVISI (U.). The Camphor Group	i, 660
BARBIER (P.). Dextrogyrate Licareol	i, 661

	PAGE
BARBIER (P.). Constitution of Rhodinol	i, 661
MARKOVNIKOFF (V.) and A. REFORMATSKY. Bulgarian (Turkish) Oil of Roses	i, 662
BARBIER (P.). Geraniol	i, 664
KLEIN (J.). Santonin	i, 664
GRASSI-CRISTALDI (G.). Oxidation Products of the Santononic acids. Diparaxylyl and Diphenyl	i, 665
CANNIZZARO (S.) and P. GUCCI. Derivatives of Photosantonin acid	i, 665
KILIANI (H.). Preparation of Pure Digitorin	i, 665
KILIANI (H.). Derivatives of Digitogenin	i, 665
BERKENHEIM (A.). Crystalline Substance from <i>Santalum Praesii</i>	i, 666
LÜDY (F.). Gum Benzoin from Siam	i, 666
GARELLI (F.). A Ketone obtained from Ethylic Dihydrocollidinedicarb- oxylate	i, 667
GHIBA (A.). Cryoscopic Behaviour of some Acetates of Feeble Bases	i, 667
CLAUS (A.). Derivatives of Quinoline	i, 667
CLAUS (A.) and M. SCHÖLLER. 1-Chloroquinoline	i, 668
CLAUS (A.) and H. HOWITZ. 1-Bromoquinoline	i, 668
CLAUS (A.) and P. GRAU. Iodoquinolines	i, 669
CLAUS (A.) and C. MASSAU. 2-Nitroquinoline and its Derivatives	i, 670
GRAEBE (C.) and A. PHILIPS. Hydroxy-derivatives of Anthraquinoline- quinone	i, 670
SEVERINI (O.). Pyrazole Compounds	i, 671
BALBIANO (L.). Phenylethyl dimethylpyrazole.	i, 672
BALBIANO (L.) and G. MARCHETTI. Syntheses of Homologues of 1-Phenyl- pyrazole	i, 672
MARCHETTI (G.). Reduction of Substituted 1-Phenylpyrazoles	i, 673
BALBIANO (L.) and O. SEVERINI. Some Acids of the Pyrazole Series	i, 673
MARCHETTI (G.). Pyrazole-3 : 5-dicarboxylic acid	i, 674
BALBIANO (L.). Platopyrazole Compounds	i, 674
STOEHR (C.). Pyrazines and Piperazines. A Reply	i, 675
ÉTARD (A.). Constitution of Nicotine. Acetylnicotine	i, 675
SCHMIDT (E.) and W. GÖHLICH. Codeine	i, 675
HESSE (O.). Quinine, Cinchonidine, and Conchinine	i, 676
HESSE (O.). Cinchonine	i, 677
LÉGER (E.). Benzoylcinchonine	i, 678
JUNGFLEISCH (E.) and E. LÉGER. Cinchonibine	i, 679
HESSE (O.). Hyosine and Oscine	i, 679
PLANTA (A. v.) and E. SCHULZE. Organic Bases in the Tubers of <i>Stachys</i> <i>tuberifera</i>	i, 679
SABANÉEFF (A.). Cryoscopy of Albumose and Peptone	i, 680
KOSSEL (A.) and J. HORBACZEWSKI. Nucleinic acid	i, 680
NICKEL (E.). Determination of Stereoisomerides	i, 681
MEYER (L.). Köhnlein's Method of preparing Paraffins. Properties of Propane	i, 681
ERDMANN (H.). Oxidation of Chloroform. Preparation of Carbon Oxy- chloride from Carbon Tetrachloride	i, 681
MOUREU. Acrylonitrile	i, 682
KESSLER (A.). Action of Iodine on Sodium Propoxide	i, 682
GASCARD (A.). Myricyl Alcohol	i, 683
AULARD (A.). Raffinose and its Decomposition Products.	i, 683
ROUVIER (G.). Combination of Iodine with Starch.	i, 683
GRIESSMAYER (V.). Dextrin	i, 684
SCHULZE (E.) and S. FRANKFURT. Occurrence of Betaïne and Choline in the Sprouts of Barley and Wheat	i, 684
BAUMANN (E.). Oxidation of the two Trithioacetaldehydes	i, 684
SEMMLER (F. W.). Citronellaldehyde	i, 685
MULDER (E.). Ketonic Compound from Tartaric acid	i, 685
WALTER (J.). Ethylic Orthoformate	i, 686
KLEBS (E.). Diamidopropionic acid	i, 686

	PAGE
TRIPPIER (J.). Preparation of Normal Caproic and Hexylic acids . . .	i, 687
REISSERT (A.). Di- γ -amidodipropylacetic acid and Octohydro-1 : 1'-naphthyridine . . .	i, 687
MOUREU. Action of Acrylic Chloride on Alcohols and Phenols . . .	i, 688
MOUREU. Acrylic Anhydride . . .	i, 688
FITTIG (R.). Constitution of the Unsaturated Acids obtained by boiling the Unsaturated $\beta\gamma$ -acids with Soda . . .	i, 688
WOLFF (L.). Constitution of Dibromolevulinic acid. . .	i, 689
STRÖM (T.). Action of Sodium Ethoxide and Ammonia on Isocapro-lactone . . .	i, 690
FITTIG (R.). Aticonic acids, New Isomerides of the Itaconic, Citraconic, and Mesaconic acids . . .	i, 691
FARCHY (J. M.) and J. TAFEL. Isomeric Diamidosuccinic acids . . .	i, 692
HJELT (E.). Anhydride Formation in the case of Substituted Succinic acids . . .	i, 693
PERKIN (W. H., Jun.). Tetramethylene Derivatives . . .	i, 693
HAWORTH (E.) and W. H. PERKIN, Jun. Synthesis of Pentamethylene-carboxylic, Hexamethylenecarboxylic (Hexahydrobenzoic), and Azelaic acids . . .	i, 694
MOUREU. Acrylamide . . .	i, 695
MOUREU. Substituted Acrylamides . . .	i, 695
REYCHLER (A.). Preparation of Urea . . .	i, 696
SCHROETER (G.) and M. LEWINSKI. Action of Thionyl Chloride on Alkyl Carbamates . . .	i, 696
WILGERODT (C.). Iodoso- and Iodoxy-derivatives of Benzene . . .	i, 696
FISCHER (O.) and E. HEPP. Action of Alkalis on Paranitrotoluene and on Paranitrotoluenesulphonic acid . . .	i, 697
KNOEVENAGEL (E.). Synthesis of Phenols from Ethylic Acetoacetate . . .	i, 697
ZINCKE (T.) and F. KÜSTER. Action of Chlorine on Catechol and Orth-amidophenol . . .	i, 698
NIEZTKI (R.) and F. MOLL. Dinitrocatechol and its Conversion into Nitranilic acid . . .	i, 699
NIEZTKI (R.) and F. MOLL. Derivatives of Phloroglucinol . . .	i, 699
CLAUS (A.). Parachlororthotoluidine . . .	i, 699
JEDLIČKA (K.). Action of Ethylenediamine on Nitrophenols, their Ethers and corresponding Halogen Derivatives . . .	i, 699
SCHALL (C.). Molecular Weight of the Carbodiimides . . .	i, 701
MÖHLAU (R.) and R. BERGER. Introduction of the Phenyl Group into Cyclic Compounds . . .	i, 701
ROTHENBURG (R. v.). Reaction of Hydrazine Hydrate with Nitro-, Nitroso-, and Isonitroso-groups . . .	i, 701
MICHAELIS (A.) and G. SCHRÖTER. Thionylbenzylhydroxylamine and Dibenzoxy-carbamide . . .	i, 702
MICHAELIS (A.) and W. JACOBI. Thionylamines of Unsaturated Bases. Thionylphenylpropylamine . . .	i, 702
MICHAELIS (A.), G. SCHRÖTER, and E. LINOW. Action of Thionyl Chloride on Benzylamine and its Homologues. Derivatives of the latter . . .	i, 703
MICHAELIS (A.) and K. LUXEMBOURG. Derivatives of Unsymmetrical Allylphenylhydrazine and Allyltolylhydrazine . . .	i, 704
MICHAELIS (A.). Action of Chlorides of Bibasic Acids on Hydrazines . . .	i, 705
MICHAELIS (L.). Bromination of Aromatic Hydrazines and Amines . . .	i, 705
BECKMANN (E.). Benzylbenzaldoxime . . .	i, 706
GOLDSCHMIDT (H.) and W. H. VAN RIETSCHOTEN. Action of Isocyanides on Aromatic Aldoximes . . .	i, 707
GOLDSCHMIDT (H.) and W. H. VAN RIETSCHOTEN. Isomerism of the Orthonitrobenzaldoximes . . .	i, 709
DOLLFUS (W.). Hydrocinnamaldoxime . . .	i, 710
HANTZSCH (A.) and A. WERNER. Stereoisomerism of the Benzhydroxamic acids . . .	i, 710
PINNER (A.). Action of Hydrazine on Imido-ethers. . .	i, 710

	PAGE
FISCHER (E.) and W. L. JENNINGS. Constitution of Hydrocyanorosaniline and of Magenta	i, 711
BÜLOW (K.). Action of Amides on Benzaldehyde	i, 712
MEYER (V.). Iodoso-compounds	i, 713
EINHORN (A.) and R. WILLSTÄTTER. Hydrogenised Paratoluic acids	i, 713
BAYER (A.) and V. VILLIGER. Hexahydroisophthalic acid	i, 713
WISLICENUS (W.). Action of Benzaldehyde on Ethylic Oxalacetate	i, 714
MAGNUS-LEVY (A.). Action of Formaldehyde on Benzenesulphonamide	i, 714
JESURIN (J. A.). Action of Phosphoric Chloride on Orthobenzoic-sulphinide	i, 715
FAHLBERG (C.). Action of Phosphoric Chloride on Orthobenzoic-sulphinide	i, 716
PERKIN (W. H., Jun.) and G. RÉVAY. Synthesis of Indene and Hydri-ndene	i, 716
ZANETTI (C. U.). Conversion of Carbazole into Indole	i, 717
HESSE (O.). Hydrocoton and its Derivatives	i, 718
CLAUS (A.) and J. BECKENKAMP. Phenylacridines	i, 718
BILTZ (H.). The Aluminium Chloride Synthesis	i, 718
BILTZ (H.). Action of Chloral on Benzene in the presence of Aluminium Chloride	i, 718
FRIEDLAENDER (P.) and A. STANGE. Phthaleinoxime	i, 719
COHN (G.). Condensation Products of Monobasic Acids with Resorcinol	i, 719
FISCHER (O.) and E. HEPP. Fluoresceïn-anilide	i, 721
FISCHER (O.) and E. HEPP. Naphthyl Red and Magdala Red	i, 721
PICTET (A.) and E. PATRY. Phenanthridone	i, 722
BAYER (A.). Orientation in the Terpene Series	i, 722
GOLDSCHMIDT (H.). Carvole	i, 723
WALLACH (O.) and M. KUTHE. Isomeric Menthylamines	i, 724
WALLACH (O.) and A. BINZ. Optical Rotatory Powers of certain Com-pounds of the Fenchylamine and Menthylamine Series	i, 725
SPIZZICHINO (E.). Essence of <i>Eucalyptus globulus</i>	i, 726
BOUCHARDAT (G.) and OLIVIERO. Essence of <i>Eucalyptus</i>	i, 726
BERTRAND (G.). Essence of Niaouli	i, 727
SCHOOR (W. K. J.). Anemonin and its Occurrence	i, 727
ZOPF (W.). Crystalline acid from Lichen. Thamnic acid	i, 727
BAMBERGER (E.). Valency of Nitrogen in Pyrroline	i, 727
MARCKWALD (W.). Amido- and Nitro-derivatives of Pyridine	i, 727
EPHRAIM (J.). Amido-derivatives of Quinoline	i, 727
CLAUS (A.). Alkyl- and Alkylene-derivatives of Substituted Cinchonic acids	i, 728
CLAUS (A.) and F. STOHR. Alkyl Derivatives of Quininic acid	i, 728
WOLFF (L.). Pyrazines and Piperazines	i, 729
ROTHENBURG (R. v.). Derivatives of Pyrazolone	i, 729
CLAUS (A.) and B. BÜTTNER. Alkyl Derivatives of 2'-Phenyleinchonic acid	i, 731
ROTHENBURG (R. v.). Pyridazolone	i, 732
GABRIEL (S.) and G. PINKUS. Phthalazine	i, 732
MEYER (L., Jun.). Ditolyleneazone	i, 733
GABRIEL (S.) and G. PINKUS. Amidoketones	i, 734
PINNER (A.). Pyrimidines free from Oxygen	i, 735
EPHRAIM (J.). Derivatives of Kyanidine	i, 735
KRÜGER (M.). Constitution of Hypoxanthine and Adenine	i, 736
PINNER (A.). Constitution of Nicotine	i, 736
ÉTARD (A.). Benzoynicotine	i, 736
SKRAUP (Z. H.). Transformations of Quinine	i, 737
SKRAUP (Z. H.) and F. K. v. NORWALL. New Isomerides of the Eth-iodides of the Cinchona Alkaloids	i, 738
LIPPMANN (E.) and F. FLEISSNER. Allocinchonine	i, 738
EINHORN (A.) and L. FISCHER. Dihydroxytropidine	i, 738
HESSE (O.). Melting Point of Cocaine Hydrochloride	i, 738

	PAGE
LADENBURG (A.). Crystalline Form of Scopoline Platirochloride . . .	i, 739
SOLDAINI (A.). The Deliquescent Alkaloid from <i>Lupinus albus</i> . . .	i, 739
VAN RYN (J. J. L.). Carpaïne	i, 740
FERREIRA DA SILVA (S. J.). Reaction of Eserine. Green Colouring Matter derived from Eserine	i, 741
KÜHNE (W.). Albumose and Peptone	i, 741
OSBORNE (T. B.) and C. G. VOORHEES. Proteïds of Wheat	i, 741
ARTHUS (M.) and A. HUBER. Solutions of Fibrin	i, 743
NENCKI (M.). Composition of Hæmatin and Hæmatoporphyrin	i, 743
EGOROFF (I. V.). Wheat Diastase	i, 743
EGOROFF (I. V.). Reychler's "Artificial Diastase".	i, 744
LUBAVIN (N.). Diastase	i, 744
GÉRARD (E.). Ferment in <i>Penicillium glaucum</i> resembling Emulsin	i, 744

INSTRUCTIONS TO ABTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

1. Before beginning to write an abstract, it is desirable to read through the whole of the original paper, in order to form a judgment as to its importance, and as to the scale on which the abstract should accordingly be made.

2. The abstract should mainly consist of the expression, in the abstractor's own words, of the substance of the paper.

3. The abstract should be made as concise as possible, consistently with a clear and accurate statement of the author's results or theories, due regard being paid to their import.

4. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should as a rule be made of this fact. Important references to the researches of others quoted by an author should be reproduced in the abstract. Always employ figures instead of Roman numerals for references, thus:—*Annalen*, 221, 92, instead of ccxxi, 92.

5. If an abstractor is acquainted with papers previously published by other authors containing statements either practically identical with, or opposed to, those in the paper abstracted, and to which no reference is made, he should notice their agreement or contradiction in a foot-note.

6. As a rule, details of methods of preparation or analysis, or generally speaking of work, may be omitted, unless such details are essential to the understanding of the results, or have some independent value.

Nomenclature.

7. Employ names such as *sodium chloride*, *potassium sulphate*, *ethyl acetate*, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chloride, sulphurous and sulphuric acid.

8. Term compounds of metallic and alcoholic radicles with the group OH, *hydroxides* and not hydrates; for example, potassium hydroxide, phenyl hydroxide, the name hydrate being reserved for compounds supposed to contain water of combination or crystallization. Compounds such as CH_3ONa , $\text{C}_2\text{H}_5\text{ONa}$, $\text{C}_7\text{H}_{15}\text{ONa}$, &c., should be termed sodium methoxide, ethoxide, heptyloxide, &c.

9. Apply the term *acid* only to compounds of hydrogen with negative radicles, such as HNO_3 , H_2SO_4 , H_3PO_4 , and denote the oxides which form acids by names such as sulphuric anhydride, carbonic anhydride. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as hydrogen sodium sulphate, hydrogen disodium phosphate, &c., to the acid salts. Basic salts are as a rule best designated merely by their *formulae*.

10. Use names such as *methane*, *ethane*, &c., for the normal paraffins or hydrocarbons of the $\text{C}_n\text{H}_{2n+2}$ series of the form $\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{CH}_3$, &c. The isomeric hydrocarbons are usually most conveniently represented by names indicating their relation to methane; for example, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3 = \text{propylmethane}$; $\text{CH}_3\cdot\text{CH}(\text{CH}_3)_2 = \text{isopropylmethane}$ or trimethylmethane; or, although less frequently, by names such as diisopropyl.

11. Term the hydrocarbons C_2H_4 and C_2H_2 *ethylene* and *acetylene* respectively (not ethene and ethine). Distinguish the homologues of ethylene, whenever possible, by names indicating their relation to it, such as methylethylene, dimethylethylene, &c., denoting the di-derivatives of the form $\text{C}_n\text{H}_{2n+1}\cdot\text{CH}:\text{CH}\cdot\text{C}_n\text{H}_{2n+1}$ as α -, and those of the form $\text{CH}_2\cdot\text{C}(\text{C}_n\text{H}_{2n+1})_2$ as β -compounds, thus: $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CH}_3 = \alpha\text{-dimethylethylene}$; $\text{CH}_2\cdot\text{C}(\text{CH}_3)_2 = \beta\text{-dimethylethylene}$. Similarly, use names such as methylacetylene and dimethylacetylene for the homologues of acetylene of the form $\text{CH}:\text{C}\cdot\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n+1}\cdot\text{C}:\text{C}\cdot\text{C}_n\text{H}_{2n+1}$. Adopt the same *allene* for the hydrocarbon $\text{CH}_2:\text{C}:\text{CH}_2$, and indicate the relation which its homologues bear to it in the same manner as pointed out for acetylene.

12. Distinguish all alcohols, that is, hydroxyl-derivatives of hydrocarbons, by names ending in *ol*; such as quinol, catechol, resorcinol, saligenol, glycerol, erythrol, mannitol, instead of hydroquinone, pyrocatechin, resorcin, saligenin, glycerin, erythrite, mannite. Compounds which are not alcohols, but which are at present distinguished by names ending in *ol*, may be represented by names ending in *ole*, if a systematic name cannot be given. For example, write indole instead of indol; furfuraldehyde instead of furfurol; fucusaldehyde instead of fucsol. Ethers derived from phenols, such as $\text{C}_6\text{H}_5\cdot\text{OCH}_3$, &c., hitherto called anisol, anethol, &c., may be distinguished by names ending in *oil*, as anisoil and anethoil.

Alcohols should be spoken of as mono-, di-, tri-, or *n-hydric*, according to the number of OH groups.

13. Compounds analogous to the acids of the lactic series containing the group OH should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups $\text{C}_2\text{H}_5\text{O}$, $\text{C}_6\text{H}_5\text{O}$, $\text{CH}_3\cdot\text{COO}$, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy-derivatives. Thus

ethoxypropionic acid instead of ethyl-lactic acid; 3 : 4 diethoxybenzoic acid instead of diethylprotocatechuic acid; and acetoxypropionic acid instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen-atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6H(C_2H_5)_2(OH)_2\cdot COOH$, and not $C_6H_3(OC_2H_5)_2\cdot COOH$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2\cdot COOH$.

14. The term *ether* should be restricted to the oxides of hydrocarbon radicles, and the so-called compound ethers should be represented by names similar to those given to the analogously constituted metallic salts (comp. 12).

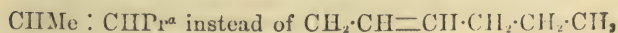
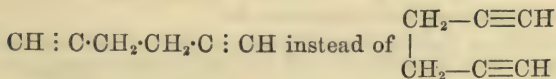
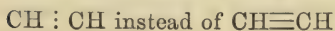
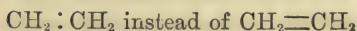
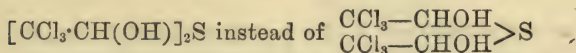
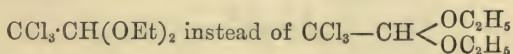
15. Compounds of the radicle SO_3H should, whenever possible, be termed *sulphonic acids*, or failing this, *sulpho-compounds*: as benzene-sulphonic acid, sulphobenzoic acid, and not sulfi-compounds. Compounds of the radicle $SO_2\cdot NH_2$ should be termed *sulphonamides*.

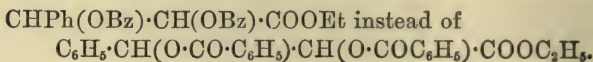
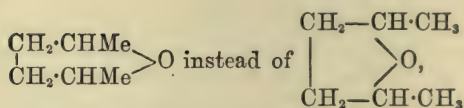
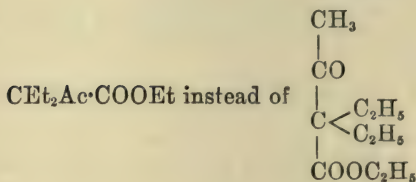
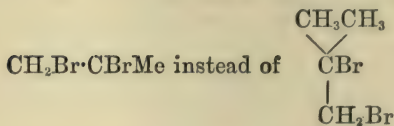
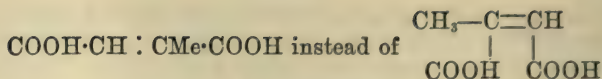
16. Basic substances should invariably be indicated by names ending in *ine*, as aniline, instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide, or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

Notation.

17. Equations should *be omitted* unless essential to the understanding of the results; they, as a rule, should *not* be written on a separate line, but should "run on" with the text.

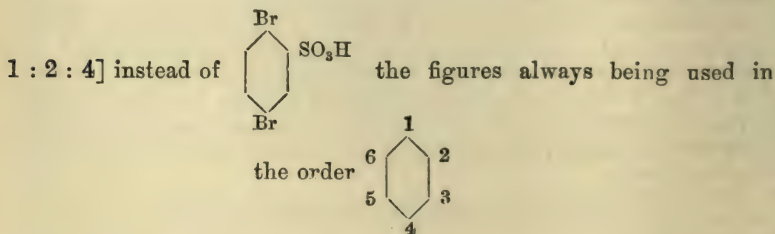
18. To economise space, it is desirable: 1, that *dots* should be used *instead of dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula; 2, that formulæ should be shortened by the judicious employment of the symbols Me for CH_3 , Et for C_2H_5 , Pr^a for $CH_2\cdot CH_2\cdot CH_3$, Pr^s for $CH(CH_3)_2$, Ph for C_6H_5 , Ac for $CO\cdot CH_3$, and Bz for $CO\cdot C_6H_5$; and 3, that formulæ should be written *in one line* whenever this can be done without obscuring their meaning. For example:





19. In representing the constitution of benzene-derivatives, as a rule, merely indicate the relative positions of the radicles in the symbol of benzene by figures, instead of by means of the hexagon symbol, for example:—

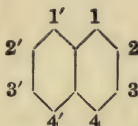
Paradibromobenzenesulphonic acid, $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{SO}_3\text{H}$ [$\text{Br} : \text{SO}_3\text{H} : \text{Br} =$



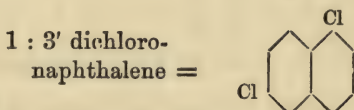
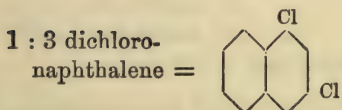
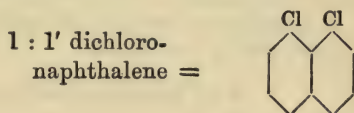
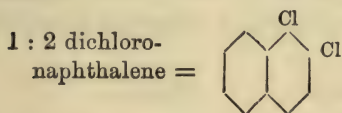
Relatively to the position 1, the positions 2 and 6 should always be spoken of as *ortho*-positions, 3 and 5 as *meta*-positions, and 4 as the *para*-position. It is better, however, in speaking of the derivatives of benzene, to express their constitution by giving them names such as 1 : 2 dibromobenzene, 1 : 3 dibromobenzene, &c., rather than by terming them *ortho*- or *meta*-dibromobenzene, &c.

20. Moreover, in representing the constitution of derivatives of other "closed-chain" hydrocarbons do not, as a rule, employ graphic formulæ, but merely indicate the position of the radicles introduced in the following manner:—

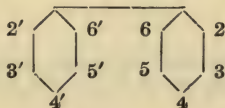
In the case of *naphthalene*, express the position of the radicles introduced in place of hydrogen relatively to the carbon-atoms common to the two "rings," and number the positions in the one ring 1, 2, 3, 4, and those in the other 1', 2', 3', 4' in the order shown by the annexed symbol:—



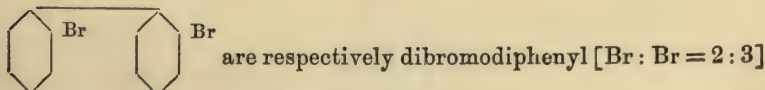
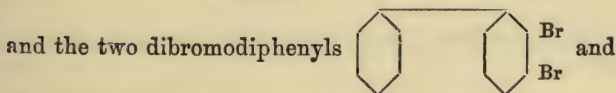
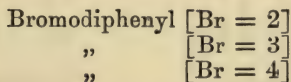
The dichloronaphthalenes, for example, are spoken of simply as 1 : 2 dichloronaphthalene, or dichloronaphthalene[Cl : Cl = 1 : 2], &c., thus:—



In the case of *diphenyl*, indicate the position of the radicles relatively to the carbon-atom of one C_6 group which is associated with the other C_6 group, and number the positions in the one group by the figures, 2, 3, 4, 5, 6, and the corresponding positions in the other group by the figures 2', 3', 4', 5', 6'. as shown by the following symbol:

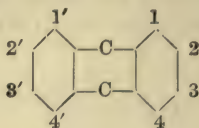


Thus the mono-derivatives, the bromodiphenyls, for example, are represented as



and dibromodiphenyl [Br : Br = 2 : 6'].

In the case of *anthracene*, employ the following symbol, and indicate the position of the radicles relatively to the central C_2 -group:



Examples:

Alizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 2].

Quinizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 4].

Anthraflavic acid, $C_6H_3(OH) : C_2O_2 : C_6H_3(OH)$ [OH : OH = 2 : 3].

Purpurin, $C_6H_4 : C_2O_2 : C_6H(OH)_3$ [OH : OH : OH = 1 : 2 : 4].

In speaking of compounds such as these, their constitution may be represented by the names

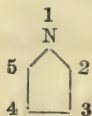
- | | |
|-----------------------------------|----------------------|
| 1 : 2 Dihydroxyanthraquinone | = Alizarin. |
| 1 : 4 „ | = Quinizarin. |
| 2 : 3' „ | = Anthraflavic acid. |
| 1 : 2 : 4 Trihydroxyanthraquinone | = Purpurin. |

Always include the letters and figures indicating the constitution of derivatives of closed-chain hydrocarbons in square brackets.

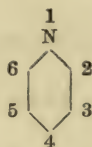
21. In the case of *thiophen*, express the position of the radicles introduced relatively to the sulphur-atom by numbers, as shown by the following symbol:



In the cases of *pyrroline* and *pyridine*, indicate the position relatively to the nitrogen-atoms as shown by the following symbols:

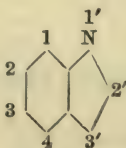


Pyrroline.

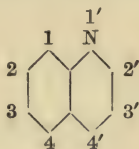


Pyridine.

In the case of *indole*, positions should be numbered as shown in the following symbol:—



In the case of quinoline, express the positions relatively to the carbon-atoms common to the two rings, and number the positions in the carbon ring 1, 2, 3, 4, and those in the nitrogen ring 1', 2', 3', 4' in the order shown by the annexed symbol:—



The Editor's decision, in all matters connected with the Abstracts, must be considered final.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Mechanical Comparison between the Cyanogen Radicle and the Halogens. By G. HINRICHS (*Compt. rend.*, 115, 177—179).—The author finds that the boiling points of cyanogen derivatives of the paraffins may be calculated correctly by means of the formulæ which he has given in former papers, if cyanogen is regarded as having the constitution usually assigned to it. In dealing with the haloïd derivatives, the halogens must be treated as simple atoms, and not as compound radicles, and the author, therefore, concludes that the chemical elements, if in reality complex in nature, cannot be compounds of the same order as the ordinary compound radicles.

H. C.

Action of Hydriodic Acid on Carbon Tetrachloride. By B. WALFISZ (*Bull. Soc. Chim.* [3], 7, 256—257).—When carbon tetrachloride (1 mol.) is heated with concentrated aqueous hydriodic acid (1 mol.) in a sealed tube for 10 hours at 130°, it is converted into iodoform and hydrogen chloride, iodine being set free. The iodine may be taken up with potash solution, or the iodoform may be distilled from the crude product.

JN. W.

Action of Zinc on Bromo-derivatives of Tricarbon Nuclei. By LESPIEAU (*Bull. Soc. Chim.* [3], 7, 260—261).—*Symmetrical tribromopropylene*, $\text{CHBr}:\text{CBr}\cdot\text{CH}_2\text{Br}$, is made by treating tetrabromallene (m. p. 9—10°) with dry potash (2 mols.) under reduced pressure. It

boils at 109—112° under a pressure of 20 mm., and attacks the eyes and skin. When poured drop by drop (15 grams) into a mixture of zinc powder (10 grams) and alcohol (10 grams of 80 per cent.) heated at 60—70°, it is converted into allylene. Tribromhydrin and allyl bromide are converted into propylene under similar conditions, and β -epibromhydrin is converted into a mixture of propylene and allylene.

JN. W.

Action of Iodine on Derivatives of Acetylene. By A. PERATONER (*Gazzetta*, 22, ii, 86—94).—The author is of opinion that hydrocarbons containing the group $\cdot\text{C}:\text{CH}$ combine readily with iodine at low temperatures, and that hydrocarbons in which the acetylenic hydrogen is displaced by organic radicles do not easily take up iodine, just as they do not form metallic derivatives (compare Liebermann and Sachse, *Abstr.*, 1892, 470). The author has prepared the compounds described below, in order to support this view.

A satisfactory yield of crotonylene is obtained on heating a solution of β -butylene dibromide (50 grams) and potash (100 grams), in absolute alcohol (150 c.c.), in an autoclave at 120° for two hours under 7 atmospheres pressure. The product is fractionated, and the vapours condensed in a freezing mixture. *Crotonylene diiodide*, $\text{CMeI}:\text{CMeI}$, is prepared by leaving a mixture of crotonylene (10 grams), alcohol (10 c.c.), and iodine (50 grams) in a sealed tube for 10 to 12 days. The product, after washing with dilute sulphurous acid and drying, ultimately solidifies with development of heat; it separates from alcohol or dilute acetic acid in colourless, tabular crystals, and melts at 41.5°. Under ordinary pressure, it boils at 180—190° with the liberation of much iodine; under a pressure of 22 mm., it boils at 108—110°, giving a slightly coloured distillate. It has an irritating odour recalling that of raspberries, and gives a normal molecular weight by the cryoscopic method in acetic acid solution.

Diphenyldiacetylene tetriodide, $\text{CPhI}:\text{CI}:\text{CI}:\text{CPhI}$, is prepared by allowing a solution of diphenyldiacetylene (2 grams), and iodine (5 grams) in carbon bisulphide (20 c.c.) to remain for eight days. The solvent is then distilled off, and the residue decolorised by sulphurous anhydride and extracted with alcohol, which leaves the iodide (0.8—1.1 gram) undissolved. It crystallises in beautiful, yellowish needles, melts at 144°, and decomposes at 150—155°. It is very sparingly soluble in the ordinary solvents, and is altered by light.

Phenylethylacetylene diiodide, $\text{CPhI}:\text{CEtI}$, may be obtained either by allowing a solution of phenylethylacetylene (3 grams) and iodine (6 grams) in alcohol (20 c.c.) to remain for two months, or by heating the mixture in a sealed tube at 100° for eight hours. It boils at 140—144° with slight decomposition and always contains free iodine; it has a sharp, aromatic odour, and does not solidify in a mixture of ice and salt.

Propylacetylene diiodide, $\text{CPrI}:\text{CHI}$, is formed with development of heat on adding iodine (40 grams) to a mixture of propylacetylene (10 grams) with alcohol (3 vols.), surrounded by a freezing mixture.

After two hours, the iodide separates as a heavy oil, which, when washed, decolorised, and dried, boils with slight decomposition at 130—133° under a pressure of 22 mm. It has an irritating odour, and is changed by light. W. J. P.

Some Derivatives of Glycerol. By A. BIGOT (*Ann. Chim. Phys.* [6], 22, 433—495).—Although this paper is very long, it contains little that is new; many of the experiments, which are described at considerable length, gave negative or indefinite results.

Hexylene dioxide, $\begin{array}{c} \text{O} \\ | \\ \text{CH}_2 \end{array} \text{---} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \text{---} \begin{array}{c} \text{O} \\ | \\ \text{CH}_2 \end{array}$, is formed, together with compounds of higher boiling point, when epichlorhydrin is treated with sodium in ethereal solution; it is isolated by repeated fractional distillation (compare Hübner and Miller, *Annalen*, 154, 186; Claus, *Ber.*, 1877, 556; and Hanriot, *Ann. Chim. Phys.* [5], 17, 96). It is a colourless liquid, boils at 153°, and is soluble in 20 parts of boiling water, but insoluble in cold water; it combines with sodium hydrogen sulphite and with magnesium chloride, and reduces ammoniacal silver nitrate and Fehling's solution. It combines with chlorine and with bromine, yielding with the latter a solid, colourless substance, which is insoluble in all ordinary solvents. On reduction with sodium amalgam in dilute alcoholic solution, or with sodium and absolute alcohol, it yields a mixture of products from which a pure compound cannot be isolated by fractional distillation. It does not combine with cold water, but when heated with dilute sulphuric acid at 100°, it is converted into *hexylene glycol oxide*, $\text{C}_6\text{H}_{12}\text{O}_3$; this compound is a colourless, moderately mobile liquid, boils at 145° under a pressure of 20 mm., and is soluble in water, alcohol, and ether; it does not combine with water even in presence of sulphuric acid. The *diacetate*, $\text{C}_6\text{H}_{10}\text{O}(\text{OAc})_2$, is formed when the dioxide is heated at 180° for 15 hours with excess of acetic anhydride or glacial acetic acid; it is a colourless liquid, boils at 141° under a pressure of 15 mm., and is insoluble in water, but soluble in alcohol, ether, chloroform, &c.; it is not acted on by acetic anhydride at 180°. The *chlorhydrin*, $\text{C}_6\text{H}_{10}\text{OCl} \cdot \text{OH}$, can be obtained by passing hydrogen chloride into well cooled hexylene dioxide; it is a colourless liquid, specifically lighter than water, in which it is only sparingly soluble, and when treated with potash, it is reconverted into the dioxide. The *bromhydrin*, $\text{C}_6\text{H}_{10}\text{OBr} \cdot \text{OH}$, and the *iodhydrin*, $\text{C}_6\text{H}_{10}\text{OI} \cdot \text{OH}$, prepared in like manner, resemble the chlorhydrin in properties.

When the mixture of chloriodhydrins (1 kilo.), obtained by treating allyl alcohol with iodine chloride in well cooled aqueous solution, is dissolved in ether and finely divided dry sodium hydroxide added to the warm solution in small portions at a time, a considerable development of heat occurs, and the ethereal solution becomes colourless; the various products of the reaction are separated by fractional distillation under reduced pressure, and seem to be: Allyl alcohol (about 50 grams), α -epichlorhydrin (about 50 grams), β -epichlorhydrin (about 40 grams), α -epi-iodhydrin (about 15 grams), and β -epi-iodhydrin (about 10 grams).

β -Epichlorhydrin, $O < \begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix} > CHCl$, is best isolated from the fraction boiling at $116-132^\circ$, which contains also α -epichlorhydrin, by heating the mixture at 100° for half an hour with dilute acid; the unchanged β -compound is extracted from the neutralised solution by shaking with ether, and purified by fractional distillation. It boils at $132-134^\circ$, is specifically heavier than water, and is not acted on by potassium cyanide in aqueous solution even at 100° . When treated with potassium acetate or silver acetate, it is slowly converted into compounds of high boiling point; with phosphorus pentachloride, it gives dichloropropylene, $CH_2Cl \cdot CCl \cdot CH_2$, and on reduction with sodium amalgam in aqueous solution, it is converted into allyl alcohol.

When symmetrical dichlorhydrin is treated with sodium in ethereal solution, sodium chloride is deposited, propylene and hydrogen are evolved, and there remains in solution a mixture of allyl alcohol, α -epichlorhydrin, and unchanged dichlorhydrin; α -monochlorhydrin, under the same conditions, gives hydrogen, glycide, and other products.

Glycide boils at $160-161^\circ$ with decomposition, and combines with water even at the ordinary temperature; when treated with hydrogen chloride, it is converted into chlorhydrin, and when heated with acetic anhydride at 170° for 12 hours, it is transformed into triacetin. It is readily acted on by acetic chloride in ethereal solution yielding two acetylchlorhydrins boiling at 218° and 230° respectively.

Diacetylchlorhydrin, $OAc \cdot CH_2 \cdot CH(OAc) \cdot CH_2Cl$, is not acted on by sodium even at 120° ; acetyldichlorhydrin, $CH_2Cl \cdot CH(OAc) \cdot CH_2Cl$, is readily acted on by sodium yielding allyl acetate; acetylchlorhydrin, $OAc \cdot CHCl \cdot CH_2 \cdot OH$, is acted on by sodium in ethereal solution with liberation of hydrogen and formation of glycide acetate (b. p. $167-169^\circ$).

F. S. K.

Characterisation of Sugars. By O. LOEW (*Landw. Versuchs-Stat.*, 41, 131-135).—The author criticises Tollens' theory as to true sugars being such only as yield levulinic acid when boiled with hydrochloric acid (Abstr., 1892, 249). He refutes Tollens' statement that his crude formose is methylanitan, and that of Fischer that methose is identical with α -acrose.

N. H. M.

Formation of Dextrose from Starch. By C. J. LINTNER (*Chem. Centr.*, 1892, i, 740; from *Zeit. Brauwesen*, 15, 123-124).—According to Cuisinier (Abstr., 1887, 354), there exists in the seeds of many plants a special ferment, glykase, which is able to change the soluble product formed by the action of diastase on starch into glucose. This opinion has been supported by Geduld, and is now confirmed by the author. Dextrose may be obtained in not inconsiderable quantity, by the action of dried malt on starch, but glykase appears to be present in the largest proportion in maize, and dextrose may be conveniently prepared from that grain by the following process:—A wort containing dextrin and maltose of 20 per cent. Ball. such as is

formed by the action of malt extract on starch paste at 60—63°, until the iodine reaction is no longer given, is, either directly or after boiling and subsequently cooling to 70°, mixed with not too finely ground malt (? maize), so that the liquid is full of it. The action is allowed to proceed at 60°, until the specific rotatory power of the product becomes less than $[\alpha]_D = 53^\circ$. As a rule, this complete conversion occurs in 30 hours, and at the outside takes 48 hours. The solution is then filtered, boiled with animal charcoal, again filtered, and evaporated on a water-bath until crystallisation commences.

Geduld states that the glykase in malt is present in an insoluble form; but from the investigations of the author, it appears to be present also in a soluble form.

G. T. M.

Preparation of Isomaltose. By C. J. LINTNER and G. DÜLL (*Chem. Centr.*, 1892, i, 886; from *Zeit. Brauwesen*, 15, 145—146).—250 grams of potato starch was stirred into 500 c.c. of diastase solution containing 0.5 gram of crude diastase at 55°, and the product mixed with 2 litres of water at 75°. After complete liquefaction, another 0.5 gram of diastase was added, and the solution allowed to remain at 67—69° for three hours. At this stage, the iodine reaction was reddish-brown, and the solution showed $[\alpha]_D$ about 170°. The liquid was concentrated to a syrup on a water-bath, mixed with alcohol (80 per cent. vol.), and the solution added to hot alcohol with constant stirring, altogether 100 parts of alcohol were employed for each 10 parts of solid matter contained in the syrup. Under these conditions, dextrin and isomaltose were almost the sole products. The alcoholic solution was separated from the precipitate, the alcohol distilled off, and the residue fermented, in about 20 per cent. solution with the smallest possible quantity of dried yeast (2 grams of yeast to each 100 grams of solid carbohydrate). After 12—14 hours, the solution was tested with phenylhydrazine for maltose and dextrose; but, after 20 hours at the ordinary temperature, these could no longer be recognised. The solution was filtered, boiled with animal charcoal, again filtered, evaporated to a syrup, and again precipitated with alcohol. After distilling off the alcohol, the remaining syrup was again treated with alcohol, as above, but this time of 85 per cent. vol., the proportion used being 100 c.c. of alcohol to not more than 5 grams of solid substance. After cooling, the liquid was again poured off, evaporated, and treated with 90 per cent. vol. alcohol, 100 c.c. of alcohol being employed for each 5, or, with still better results, 3 grams of dry substance. After cooling, the alcoholic solution contained isomaltose with, at the most, only a very slight trace of dextrin, and this was removed by precipitation with absolute alcohol, of which so much was added that a slight turbidity, permanent at 40°, was obtained. The solution was then poured off from the syrup and fractionally precipitated anew.

The alcohol was then distilled off and the isomaltose obtained as a syrup. The carbohydrate could not be obtained pure in the solid form by precipitation with absolute alcohol, for the alcohol adhered to it when the temperature remained below 90°, and at temperatures above 90° decomposition occurred. Perfectly dry isomaltose is a

very hygroscopic substance. In the above process, the author obtained 20 per cent. of the dried starch employed as isomaltose.

G. T. M.

Higher Nitro-derivatives of Starch. By O. MÜHLHÄUSER (*Chem. Centr.*, 1892, i, 982—983; from *Dingl. polyt. J.*, **284**, 137—143).—According to Béchamp, two isomeric tetranitro-derivatives of starch, $C_{12}H_6O_6(ONO_2)_4$, are formed when a freshly prepared, cold solution of the carbohydrate in concentrated nitric acid is mixed with sulphuric acid. On the addition of water, the two compounds are precipitated, and they may be conveniently separated by digestion with alcohol, in which only one, namely, that having its ignition point at 178° , is soluble. The compound which is not taken up by alcohol ignites at 172° . The tetranitro-derivative which dissolves in alcohol is identical with that obtained in the process of the Nobel Dynamite Company, which consists in treating a solution of starch in nitric acid with the waste acids from the manufacture of nitro-glycerin; and is also identical with the compound prepared by pouring into water a solution of starch in nitric acid which has been allowed to remain for some time. The process last named gave a very stable product.

The author has also succeeded in isolating two other nitro-derivatives of starch. A *penta-derivative*, $C_{12}H_{15}O_5(ONO_2)_5$, is obtained when 20 grams of rice starch, dried at 100° , is added in small portions at a time to a mixture of 100 grams of nitric acid (sp. gr. 1.501) and 300 grams of sulphuric acid (sp. gr. 1.8). The solution is allowed to remain for an hour, and is then poured into a large quantity of cold water. The precipitate is collected, washed, and freed from any simultaneously formed tetranitro-derivative by treatment with alcohol. The insoluble pentanitro-derivative ignites at 160° , does not colour potassium iodide paper at 60 — 70° , is insoluble in ether, and dissolves in acetone, ethyl acetate, and nitrobenzene. The existence of this pentanitro-derivative shows that the empirical formula for starch, $C_6H_{10}O_5$, must, at least, be doubled. When 40 grams of dried starch is added to 400 grams of nitric acid (sp. gr. 1.501), and, after remaining for 24 hours, 220 grams of the solution is slowly stirred into 600 c.c. of sulphuric acid at 66° , a gelatinous precipitate is obtained, which, in addition to the pentanitro-derivative, contains a *hexanitro-derivative*, $C_{12}H_{14}O_4(ONO_2)_6$. This ignites at 155° , is unstable in presence of potassium iodide at 60 — 70° , is insoluble in dilute alcohol and ether, but dissolves in ethyl alcohol, acetone, nitrobenzene, and acetic ether.

The nitro-derivatives of starch prepared with concentrated sulphuric acid are decomposed at 60 — 70° , with evolution of nitrous fumes, and are, therefore, unsuitable for blasting purposes. Their instability is, perhaps, to be attributed to the presence of a small quantity of starch containing sulphonic acid groups in the molecule. For the preparation of a nearly smokeless powder, the stable tetranitro-derivative, obtained without the aid of sulphuric acid, is best employed. It should be mixed with 3 parts of nitro-jute, kneaded with ethyl acetate, milled, and dried at 50 — 60° .

G. T. M.

Molecular Masses of Dextrin and Gum Arabic as determined by their Osmotic Pressures. By C. E. LINEBARGER (*Amer. J. Sci.* [3], **43**, 426—428).—The author has calculated the molecular weight of gum arabic and dextrin from Pfeffer's observations on the osmotic pressures of their solutions. In each case, the results indicate that the simpler molecular formulæ, which are usually taken to represent these substances, should be multiplied by seven to get the true molecular formulæ. H. C.

Action of Secondary Capryl Iodide on Trimethylamine. By H. MALBOT and A. MALBOT (*Bull. Soc. Chim.* [3], **7**, 213—214).—An ethereal solution of secondary capryl iodide (1 mol.) is shaken with an aqueous solution of trimethylamine (1 mol.) for a week or more. The ethereal layer is washed with water to remove unchanged amine, and then fractionated; caprylene passes over at 125°, and about half the original amount of capryl iodide remains unchanged, dissociating, however, at a slightly higher temperature. The aqueous layer contains unchanged trimethylamine, together with the hydriodide, from which the base is recovered by treatment with silver oxide. The formation of caprylene in the cold is evidently due to the simple transference of the elements of hydrogen iodide from the capryl iodide to the trimethylamine. JN. W.

Glycolaldehyde. By W. MARCKWALD and A. ELLINGER (*Ber.*, **25**, 2984—2985).—The authors have prepared the glycolaldehyde, $\text{OH}\cdot\text{CH}_2\cdot\text{CHO}$, recently described by Fischer and Landsteiner, by a method which gives a better yield of the substance. The starting point is Pinner's glycol-acetal (this Journal, 1872, 407), which may be readily prepared in quantity; Pinner states that the hydrolysis does not proceed smoothly with mineral acids, but the authors find that if very dilute acids be employed, the hydrolysis may be readily effected. The acetal is boiled with an equal volume of water and a few drops of hydrochloric acid or sulphuric acid, a portion of the alcohol formed being allowed to distil off. The boiling is continued until oily drops no longer separate on the addition of large quantities of water, and the product is then distilled. Alcohol first passes over, mixed with very little aldehyde, and then a mixture of aldehyde and water, the residue finally commencing to decompose. A concentrated solution of glycolaldehyde may be obtained by using sulphuric acid as the hydrolysing agent, and precipitating it with barium carbonate, after distilling off the alcohol. The authors confirm the description of the properties of glycolaldehyde given by Fischer and Landsteiner, with the exception of the extent to which it volatilises in a current of steam, which they find to be considerably greater than that observed by the latter investigators. H. G. C.

Specific Gravity of Aqueous Solutions of Acetone. By K. P. MACELROY and W. H. KRUG (*Chem. Centr.*, 1892, ii, 158; from *J. Anal. Chem.* **6**, 187—188).—The acetone employed was purified by repeated distillation over calcium chloride; it boiled at 56.4°. The table gives the specific gravity at various temperatures referred to water at 4°; the weighings were not reduced to vacuum-weighings.

Acetone per cent.	15°.	20°.	25°.	Acetone per cent.	15°.	20°.	25°.
100	0·79726	0·79197	0·78630	45	0·93518	0·93091	0·92678
95	—	0·80748	0·80205	40	0·94488	0·94075	0·93691
90	—	0·82197	0·81653	35	0·95293	0·94931	0·94547
85	—	0·83588	0·83073	30	0·96092	0·95748	0·95411
80	—	0·84981	0·84454	25	0·96783	0·96490	0·96221
75	0·86442	0·86129	0·85533	20	0·97444	0·97210	0·96961
70	0·88085	0·87545	0·87073	15	0·98038	0·97831	0·97604
65	0·89271	0·88785	0·88282	10	0·98681	0·98513	0·98342
60	0·90447	0·89953	0·89477	5	0·98921	0·99169	0·98979
55	0·91526	0·91054	0·90603	0	0·99160*	0·99826	0·99712
50	0·92549	0·92051	0·91673				

The sp. gr. of pure acetone (water at 4° = 1) at various temperatures is given below:—

15°.	16°.	17°.	18°.	19°.	20°.	21°.
0·79726	0·79620	0·79514	0·79408	0·79302	0·79197	0·79107
	22°.	23°.	24°.	25°.		
	0·78988	0·78869	0·78750	0·78630		C. F. B.

Condensation of Acetaldehyde with Acetone. By L. CLAISEN (*Ber.*, 25, 3164—3166).—The author failed to obtain ethylideneacetone by the action of dehydrating agents on a mixture of acetaldehyde and acetone, probably because of the formation of paraldehyde, which has almost the same boiling point as ethylideneacetone, and cannot, therefore, be separated from it. Acetaldehyde and acetone combine in the presence of dilute alkalis, alkali carbonates, or cyanides, forming *hydracetylacetone*, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{COMe}$, a compound intermediate between aldol and diacetonie alcohol (this Journal, 1876, i, 365), the trichloro-derivative of which has been described by Königs (*Abstr.*, 1892, 694). It is a liquid of ketone-like odour, miscible in all proportions with water, boils at 77—78° (19 mm.), and has a specific gravity at 15° = 0·978. It boils at the ordinary pressure at 176—177° with scarcely any decomposition, and yields a *hydrazone* melting at 86—87°.

Ethylideneacetone, $\text{CHMe}\cdot\text{CH}\cdot\text{COMe}$, is obtained when *hydracetylacetone* is boiled for some time with acetic anhydride. It is a colourless liquid, boiling at 122°; it has an odour resembling crotonaldehyde, but less pungent, and a specific gravity at 15° = 0·861. Experiments are in progress on the action of formaldehyde on acetone.

A. R. L.

Derivatives of Trimethylene Chlorobromide. By P. BLANK (*Ber.*, 25, 3040—3047).— γ -*Thiodibutyramide*, $\text{S}(\text{C}_3\text{H}_7\text{CONH}_2)_2$, is obtained by dropping γ -thiodibutyronitrile (Gabriel, *Abstr.*, 1890, 1221) into concentrated sulphuric acid (4 parts) cooled by ice, diluting

* This figure seems to be a misprint, probably for 0·99916.

with water, precipitating the sulphuric acid by barium carbonate, and evaporating the filtrate. It crystallises in mushroom-like aggregates of delicate needles, melts at 152° , and gives γ -thiodibutyric acid (*loc. cit.*) on hydrolysis. The latter yields on oxidation γ -sulphonedibutyric acid, $\text{SO}_2(\text{C}_3\text{H}_6\cdot\text{COOH})_3$.

Ethyl γ -cyanopropylmalonate, $\text{CN}\cdot\text{C}_3\text{H}_6\cdot\text{CH}(\text{COOEt})_2$, is formed by boiling a solution of sodium (1.19 grams) in absolute alcohol (20 c.c.) with ethyl malonate (16.3 grams) and γ -chlorobutyronitrile (9.5 grams), in a reflux apparatus for three hours, driving over the unaltered nitrile in a current of steam, and extracting the residual oil with ether. After twice fractionating, it passes over at 290 — 295° .

γ -Anilidobutyronitrile, $\text{NHPh}\cdot\text{C}_3\text{H}_6\cdot\text{CN}$, is produced when γ -chlorobutyronitrile is heated on the water-bath for three hours with aniline (3 parts); the *platinochloride* melts at 191° with decomposition.

γ -Piperidylbutyronitrile, $\text{C}_5\text{NH}_{10}\cdot\text{C}_3\text{H}_6\cdot\text{CN}$, prepared by gradually adding γ -chlorobutyronitrile (48.6 grams) to piperidine (40 grams), cooled by ice, shaking the mixture, and driving over the unaltered reagents in a current of steam, boils at 241 — 245° . The *platinochloride* melts at 171 — 172° , and the *picrate* at 113 — 115° . When the nitrile is heated with concentrated hydrochloric acid (5 parts) in a sealed tube at 100° for three hours, γ -piperidylbutyric acid, which yields a *picrate* melting at 158° , is obtained; whilst if it is dissolved in absolute alcohol (27 parts) and boiled with sodium (2 parts), δ -piperidylbutylamine, $\text{C}_5\text{NH}_{10}\cdot\text{C}_4\text{H}_8\cdot\text{NH}_2$, which boils at 225° (743 mm.), and gives a *platinochloride* melting at 215° , is formed.

When a solution of γ -phenoxybutyronitrile (Gabriel, *Abstr.*, 1892, 131) in 5 per cent. alcoholic ammonia (8 parts) is saturated with hydrogen sulphide, heated at 100° , and the solvent evaporated, ether extracts from the residue γ -phenoxybutyrothiamide, $\text{OPh}\cdot\text{C}_3\text{H}_6\cdot\text{CS}\cdot\text{NH}_2$, which crystallises from water in long needles; the smaller portion, insoluble in ether, separates from hot water in needles, melts at 176° with decomposition, and is *phenoxybutyramidine thiosulphate*, $[\text{OPh}\cdot\text{C}_3\text{H}_6\cdot\text{C}(\text{NH})\cdot\text{NH}_2]_2\cdot\text{H}_2\text{S}_2\text{O}_3$.

When δ -phenoxybutylamine hydrobromide (6 grams) is heated with fuming hydrobromic acid (20 c.c.) in a sealed tube at 150° for 4—5 hours, and the product evaporated to dryness, the residue gives pyrrolidine on distillation with potassium hydroxide solution, and by fractional precipitation with picric acid δ -bromobutylamine *picrate*, $\text{CH}_2\text{Br}\cdot\text{C}_3\text{H}_6\cdot\text{NH}_2\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, which crystallises in leaflets and melts at 105° , is obtained.

When paracresol (50 grams) and trimethylene chlorobromide (82 grams) are added to a solution of sodium (10.6 grams) in absolute alcohol (120 c.c.), the mixture warmed on the water-bath for about three hours, and water added, an oil separates; on distilling this, the main portion consisting of γ -chloropropyl paratolyl ether, $\text{CH}_2\text{Cl}\cdot\text{C}_2\text{H}_4\cdot\text{OC}_6\text{H}_4\text{Me}$, passes over at 252 — 260° (754 mm.), whilst the fraction boiling above 300° is *trimethyleneglycol diparatolyl ether*, $\text{C}_3\text{H}_6(\text{OC}_6\text{H}_4\text{Me})_2$, which crystallises from alcohol in slender, felted needles, and melts at 94° . If γ -chloropropyl paratolyl ether (33 grams) is boiled with a mixture of ethyl malonate (28.8 grams) and sodium (4.12 grams) dissolved in absolute alcohol (66 grams) for 11 hours, it

yields *ethyl paracresoxypropylmalonate*, which is converted into the *potassium salt* by heating it with 30 per cent. alcoholic potash; the corresponding *acid*, $\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{H}_6 \cdot \text{CH}(\text{COOH})_2$ melts at $116-119^\circ$. On heating the latter until the evolution of gas ceases, δ -*paracresoxyvaleric acid*, $\text{C}_7\text{H}_7\text{O} \cdot \text{C}_4\text{H}_8 \cdot \text{COOH}$, passes over at 325° ; it melts at 96° . By heating this with phosphorus pentachloride, and treating the resulting chloride with dilute ammonia, it furnishes the *amide*, $\text{C}_7\text{H}_7\text{O} \cdot \text{C}_4\text{H}_8 \cdot \text{CONH}_2$, which crystallises from dilute alcohol in long, felted needles, and melts at 152° .

When δ -*paracresoxyvaleric acid* is distilled with lead thiocyanate, the corresponding *nitrile* passes over between 296° and 310° ; it is converted into ϵ -*paracresoxyamylamine*, $\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_5\text{H}_{10} \cdot \text{NH}_2$, by treatment with the requisite amount of sodium dissolved in absolute alcohol; the *hydrochloride* melts at 188° , and the *platinochloride* at 202° with decomposition. When the last-mentioned base is heated in a sealed tube at 150° for five hours with fuming hydrobromic acid, it gives ϵ -*bromamylamine*, $\text{CH}_2\text{Br} \cdot \text{C}_4\text{H}_8 \cdot \text{NH}_2$, which is isolated by means of its *picrate* (m. p. $108-110^\circ$). A. R. L.

An Index to the Literature of Angelic and Tiglic Acids from 1842 to 1892. By H. P. TALBOT (*Technol. Quart.*, 5, Nos. 1 and 2).—A summary of the various investigations on angelic and tiglic acids, accompanying an index (both of authors and subjects) to the literature of the subject. The index is believed to be practically complete to April, 1892.

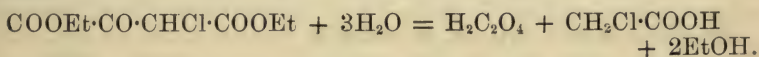
Succinic Acid. By A. RAU (*Chem. Centr.*, 1892, ii, 155—157; from *Revue Hygiene*, 14, 225—242).—The following amounts of succinic acid are dissolved at 15° by 100 parts of the solvents named:—Anhydrous ether, 1.193; alcohol, 96 per cent., 9.986; 90 per cent., 11.984; methyl alcohol, 15.73; acetone, 5.54. To estimate succinic acid in an alcoholic liquid, it is concentrated to a syrup, extracted repeatedly with boiling alcohol, the filtered extract evaporated, the residue dissolved in a little hot water, cooled, filtered, barium nitrate and 3—4 vols. of 90 per cent. alcohol added, and the whole stirred vigorously. The precipitate is collected on a filter, washed with 70 per cent. alcohol, warmed with sodium carbonate, filtered, the filtrate neutralised with nitric acid, evaporated to a small bulk, neutralised with ammonia, magnesia mixture (prepared from the nitrate) added, and the whole allowed to remain for 3—4 hours. It is then filtered, heated with potash until the ammonia is expelled, filtered, and neutralised with nitric acid. The liquid is concentrated to 100—150 c.c., precipitated with dilute silver nitrate (1:20), and the precipitate collected on a weighed filter, dried, and weighed. If the original liquid contained chlorides, these must be estimated on a separate sample, and a correction applied to the above result.

Wines examined contained from 0.317 (in a sample of Pfälzer wine) to 1.512 grams (in a sample of genuine sour Tokay) of succinic acid per litre. Experiments were made on the fermentation of 15 per cent. solutions of cane sugar, pure grape sugar, and maltose, at 15° , 25° ,

and 35°; to each 100 c.c. of the solution were added 25 c.c. of a solution of 25 grams of acid potassium phosphate, 8.5 grams of silver sulphate, and 20 grams of asparagine per litre, to serve as food for the ferment. It appears that the formation of succinic acid is not diminished by a lowering of temperature, nor is it increased by the addition of the food-solution; precisely the opposite is true of the formation of glycerol. The presence or absence of air has no effect on the formation either of glycerol or of succinic acid. The more energetic the action of the yeast cells, the more succinic acid is usually formed. It seems thus that succinic acid is a normal product of the alcoholic fermentation, and its formation does not depend on a simultaneous production of glycerol.

C. F. B.

Decomposition of the Ethyl Salts of some Chloro- β -ketonic Acids by Dilute Sulphuric Acid. By A. PERATONER (*Gazzetta*, 22, ii, 37—44).—Ethyl chloroxalacetate (30 grams), when boiled for an hour with dilute (1:5) sulphuric acid (150 c.c.) in a reflux apparatus, gives off very little carbonic anhydride. The product yields a resinous substance with phenylhydrazine, but on treating it with barium hydroxide, and subsequently removing the excess of barium, barium oxalate is obtained. The filtrate from this, after concentration, yields crystals of barium chloracetate, and on again filtering and treating with silver nitrate, a precipitate of silver chloracetate is thrown down. The hydrolysis, therefore, proceeds in accordance with the equation



Ethyl chloracetoacetate, when similarly treated, evolves much carbonic anhydride, and monochloracetone is obtained on distilling the product. On prolonged heating, the ethyl salt decomposes, with formation of monochloracetic acid.

Ethyl chlorobenzoylacetate, when treated with dilute sulphuric acid, yields *w*-chloracetophenone, which may be separated by distillation in a current of steam; the aqueous distillate also contains benzoic acid, and monochloracetic acid is produced during the hydrolysis.

W. J. P.

Specific Gravities of some Isomeric Acids. By S. TANATAR and C. TCHELEBIEFF (*J. Russ. Chem. Soc.*, 22, 548—549).—The authors have made determinations of the specific gravities of various pairs of solid isomeric acids, using a pyknometer with australene (in which the substances are insoluble) as liquid. Their results are exhibited in

Acid.	Sp. gr.	Mol. vol.
Fumaric	1.625	71.38
Maleïc	1.590	72.95
Succinic.....	1.554	75.93
Isosuccinic	1.455	81.09
Dimethylsuccinic (fumaroid)..	1.314	111.11
„ (maleïnoid)	1.339	109.03

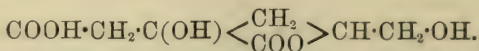
the accompanying table, the temperature of experiment being 18.5° to 20°, and water of the same temperature being chosen as standard.

J. W.

Oxidation of Diallyloxalic Acid by Potassium Permanganate.

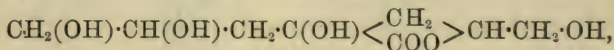
By S. PHOKIN (*J. Russ. Chem. Soc.*, **22**, 522—535).—A neutral solution of the potassium salt of diallyloxalic acid was cooled in ice, and to it there was added drop by drop a 1 per cent. solution of potassium permanganate, in such quantity that to 1 mol. of acid there were 2—3 atoms of available oxygen. On the following day, the solution was filtered from the oxide, and treated with carbonic anhydride. A portion was investigated for neutral organic substances, but none were found. The bulk of the solution was then treated with sulphuric acid, corresponding with the amount of potassium present, and distilled. The acid distillate was found to contain nothing but formic acid. In order to obtain the non-volatile substances in the solution which remained, it was extracted first of all with ether. In the ethereal extract unchanged diallyloxalic acid, oxalic acid, and some formic acid were found. The aqueous portion was now evaporated to dryness, and treated with alcohol, in which all the organic substances dissolved. In order to remove the oxalic acid, the aqueous solution of the extract was treated successively with lead carbonate and hydrogen sulphide; the filtrate from the sulphide precipitate was again evaporated to dryness and extracted with alcohol. On evaporating the alcohol, a syrupy mass was left; this was the chief product of the oxidation, and consisted of a mixture of tetrahydroxyoctolactone and a lactonic acid.

The lactonic acid, $C_7H_{10}O_6$, is probably



The calcium salt of the bibasic acid, corresponding with this lactonic acid, is very slightly soluble in water, and advantage was taken of this property in order to separate the two products of oxidation, these being boiled up with calcium hydroxide and water. In order to obtain the free lactonic acid, the calcium salt was dissolved in acetic acid, and decomposed by precipitation with oxalic acid; the solution was filtered, and the filtrate boiled to get rid of acetic acid. The oxalic acid present was then removed, and the pure lactonic acid, which forms a thick, yellow syrup, was obtained as above. Its barium salt, $Ba(C_7H_9O_6)_2$, may be obtained by treating it with barium carbonate, filtering, and precipitating with alcohol. The barium salt of the bibasic acid, $BaC_7H_{10}O_7$, is a gummy mass, whilst the calcium salt, $CaC_7H_{10}O_7$, is pulverulent, and nearly insoluble in water.

Tetrahydroxyoctolactone, $C_8H_{14}O_6$, probably



forms a syrup having a sweet taste. The calcium salt of the corresponding acid, $Ca(C_8H_{15}O_7)_2 + 2H_2O$, is soluble in water. The barium salt is a yellow, vitreous mass, and anhydrous. The acid can form basic barium and calcium salts.

Bulitch (*J. Russ. Chem. Soc.*, **19**, 73) found a tetrahydroxyoctolactone amongst the products obtained on oxidising diallyloxalic acid by means of nitric acid. The authors consider this lactone to be isomeric, and not identical, with theirs, and think it probably has the formula $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{C}(\text{OH}) < \begin{smallmatrix} \text{CH}(\text{OH}) \\ \text{COO} \end{smallmatrix} > \text{CH} \cdot \text{CH}_3$.

J. W.

Action of Bromine on Closed Chain Hydrocarbons in presence of Aluminium Bromide. By V. MARKOVNIKOFF (*Compt. rend.*, **115**, 440—442).—The author's researches lead to the conclusion that the action of bromine on naphthenes in presence of aluminium bromide at the ordinary temperature, affects chiefly the hydrogen atoms of the closed chain, and converts the open chain into a benzene ring, in which all the hydrogen atoms are displaced by bromine whilst the lateral chains remain intact. To this rule, however, the simplest naphthene, C_6H_{12} , is an exception, since it yields no hexabromobenzene. So far, results have been obtained up to C_9 only, and all attempts to obtain crystalline products from naphthenes of C_{10} and higher have failed. It would seem that the formation of crystalline products becomes more and more difficult as the complexity of the lateral chains increases; propylnaphthene, for example, yields only a very small quantity of crystalline tribromopseudocumene.

When the hydrocarbons contain only methyl groups, the reaction gives definite results, and can be used for the qualitative detection of naphthenes. A very small fragment of aluminium is allowed to burn in a test tube containing about 0.5 gram of bromine, and after the latter has cooled, 3 or 4 drops of the hydrocarbon under examination are added. There is an immediate reaction, and after the excess of bromine has been expelled by evaporation, microscopic crystals are seen, impregnated with an oily liquid.

In some cases there is transposition of the lateral chains. Octonaphthene, for instance, always yields tetrabromoparaxylylene, although in its other reactions it behaves as hexahydrometadimethylbenzene. Bromine, under the conditions indicated, acts on the derivatives of the naphthenes as well as on the naphthenes themselves.

C. H. B.

Suberene, a New Hydrocarbon. By V. MARKOVNIKOFF (*Compt. rend.*, **115**, 462—464).—Amongst the products of the action of fuming hydriodic acid on suberonyl alcohol at 280° (*Abstr.*, 1890, 728) is a hydrocarbon, C_7H_{14} , which has hitherto been regarded as heptamethylene. This hydrocarbon, however, does not yield crystalline products with bromine in presence of aluminium bromide, if the action is allowed to continue for a short time only, but if these substances are allowed to react for several days in a sealed tube, pentabromotoluene is obtained. It would seem, therefore, that the supposed heptamethylene is really hectanaphthene or hexahydrotoluene, and it would follow that suberone is probably a derivative of heptanaphthene, but this last conclusion cannot be regarded as established.

When suberonyl iodide is allowed to act on zinc for several days, with repeated addition of small quantities of hydrochloric acid, a hydrocarbon is obtained, which, after distillation over sodium, boils at

117°; sp. gr. = 0.8253. It reacts readily with bromine in presence of aluminium bromide, and after about 12 hours is converted into a crystalline mass of small needles of pentabromotoluene. The conditions under which this hydrocarbon is produced render it very improbable that any isomeric change takes place at the moment of its formation. Its high boiling point and specific gravity indicate that it belongs to a hitherto unknown series of hydrocarbons, and the author gives it provisionally the name *suberene*.
C. H. B.

Hexiodobenzene. By G. E. SHAW (*Chem. News*, 66, 141).—By heating 250 grams of iodine with 100 c.c. of pure benzene and 200 c.c. of strong sulphuric acid for a few hours daily during 10 days, a product was obtained containing, in addition to mono- and di-iodobenzene, *hexiodobenzene*; this was separated by means of its comparative insolubility in alcohol and benzene. By crystallisation from carbon bisulphide and treatment with animal charcoal it was obtained in white needles, melting at 248° (corr.); it is freely soluble in aniline and nitrobenzene.
D. A. L.

Preparation of α -Trinitrotoluene. By C. HÄUSSERMANN (*Zeit. ang. Chem.*, 1891, 661–662).—Toluene may be converted into its trinitro-derivative in a single operation; but in practice it is better to start from dinitrotoluene, which is readily obtained pure by mixing 100 parts of paranitrotoluene gradually with a mixture of 75 parts of 92 per cent. nitric acid and 150 parts of sulphuric acid. The acid mixture must be poured into the nitrotoluene, and the temperature should at first not exceed 60–65°. After all the acid has been added, the whole is heated for half an hour up to 80–85°, and the acid is then separated from the crude product. This is composed of a crystalline mass, solidifying at 69.5°, and is completely free from the mono- or tri-nitro-derivative. A formation of isomeric compounds does not take place, and even oxidation products are only present in traces; in fact, the reaction is almost quantitative.

The trinitro-derivative is obtained when the dinitro-compound is dissolved, by the aid of a gentle heat, in four times its weight of sulphuric acid, and carefully mixed with 1.5 times its weight of (92 per cent.) nitric acid, then finally heated up to 90–95°. The solution, which is at first clear, soon becomes turbid, and a layer of a clear, yellow oil accumulates on the surface and gradually increases. The reaction may be considered as finished when the slight evolution of gas completely ceases, which is generally the case after four or five hours. The operation is then stopped, and after the removal of the undecomposed acid, the residue is washed first with hot water, and finally with very weak soda solution. From 100 parts of dinitrotoluene, about 105 parts of the trinitro-product are obtained in the form of a nearly white, well crystallised mass, which in its crude state solidifies at 79°. When recrystallised from hot alcohol, its melting point is raised to 81.5°.

If, for its preparation, use is made of ordinary commercial dinitrotoluene (melting point 60–64°), the action does not proceed so quietly, and red fumes are evolved, showing a partial decomposition of the

substance. Although a pure product is finally obtained, the yield of the compound is about 10 per cent. less than in the process described, and there is also a great waste of nitric acid. It must also be remembered that trinitrotoluene is not absolutely insoluble in hot water, so that over-washing may cause serious loss. It is also slightly decomposed on prolonged treatment with alkalis or even their carbonates.

L. DE K.

Dinitrochlorotoluene and the Synthesis of Azine Dyes. By R. NIETZKI and E. REHE (*Ber.*, **25**, 3005—3009).—*Dinitrochlorotoluene*, [Me : Cl : NO₂ : NO₂ = 1 : 2 : 3 : 5] is obtained by adding ortho-chlorotoluene (1 part) to a well-cooled mixture of nitric acid (sp. gr. = 1·48, 3 parts) and concentrated sulphuric acid (9 parts). The reaction is completed by heating at 80° for a few hours, and the mixture is then poured on to ice. It crystallises from alcohol in almost colourless needles, melts at 45°, and is easily soluble in alcohol and ether. When heated with alcoholic ammonia, it yields the dinitro-orthotoluidine melting at 208°, and when boiled with alcoholic potash, it yields the dinitro-orthocresol, melting at 85°. When reduced with stannous chloride, it is converted into a *chlorotoluylenediamine*; this crystallises from water in needles, melts at 73°, and yields well crystallised salts, and a diacetyl derivative when treated with acetic anhydride. Dinitrochlorotoluene, like the corresponding benzene derivative, reacts with amines, and the chlorine atom is replaced by the amido-group. With aniline, it yields *dinitrotolylphenylamine*, which crystallises in beautiful, red plates, and melts at 169°. With paraphenylenediamine, it yields dinitrotolylamidophenylamine and tetranitroditylparaphenylenediamine.

Dinitrotolylamidophenylamine crystallises from alcohol in black needles, melts at 170°, and dissolves in hot dilute sulphuric acid, from which solution a yellow sulphate is precipitated on cooling. The *acetyl* derivative melts at 210°.

Tetranitroditylparaphenylenediamine crystallises from nitrobenzene in small, brownish-red needles, and melts above 330°.

By the action of dinitrochlorotoluene on dimethylparaphenylenediamine, a base is obtained which crystallises in brownish-black needles, is easily soluble in hot dilute mineral acids, and on reduction with stannous chloride and hydrochloric acid is easily converted into the base $\text{C}_6\text{H}_2\text{Me}(\text{NH}_2)_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$. This only differs from the leuco-base of toluylene-blue in the position of the methyl group, which in the latter is meta- relatively to the amido-group. The *hydrochloride* is very easily oxidised, and cannot therefore be obtained pure.

The *azine*, $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{Me} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{NMe}_2$, is obtained by heating the stannochloride of the preceding base (30 grams), dissolved in water (1 litre), and previously neutralised with calcium carbonate, with Weldon mud (30 grams, 60 per cent. MnO₂) on the water bath. It crystallises from dilute alcohol in beautiful needles, having a coppery lustre, and does not contain water after drying at 100°. The aqueous solution is yellowish-brown; the ethereal solution exhibits a greenish-yellow fluorescence. The salts are very similar to those of toluylene-

red, but impart a yellower shade to fibres. It dissolves in concentrated sulphuric acid forming a green solution, which on dilution turns blue and then red.

E. C. R.

Orthocyano- and Orthonitro-benzyl Chloride. By H. CASSIRER (*Ber.*, 25, 3018—3030).—*Phenoxyorthotoluonitrile*, $\text{OPh}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$, is prepared by adding orthocyanobenzyl chloride (7.65 grams) dissolved in alcohol (25 c.c.) to a solution of sodium (1.15 grams) and phenol (4.7 grams) in alcohol (30 c.c.), and heating the mixture on the water-bath until it has a neutral reaction, when the compound separates. It crystallises from light petroleum in white needles, and melts at $63\text{--}65^\circ$. The *thiamide*, $\text{OPh}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CS}\cdot\text{NH}_2$, is obtained when the nitrile (5 grams) is dissolved in alcoholic ammonia (10 c.c.), and the solution saturated with hydrogen sulphide and heated in a sealed tube at 100° for two hours. It crystallises from dilute alcohol in slender, bright-yellow needles, and decomposes when treated with zinc and hydrochloric acid. An attempt to reduce phenoxyorthotoluonitrile with zinc and hydrochloric acid was also unsuccessful, and no characteristic compounds were obtained by the action of concentrated sulphuric acid on this compound.

Ethoxyorthotoluonitrile, $\text{OEt}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$, is prepared by heating orthocyanobenzyl chloride (7.65 grams) dissolved in alcohol (20 c.c.) with a solution of sodium (1.15 grams) in alcohol (40 c.c.) on the water-bath. After distilling off the alcohol, the compound remains as an oil; it boils at 242° , and gives ψ -phthalimidine (*Abstr.*, 1887, 1038) when dissolved in cooled concentrated sulphuric acid. The *thiamide*, $\text{OEt}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CS}\cdot\text{NH}_2$ melts at 84° .

When orthocyanobenzyl chloride is dissolved in 75 per cent. acetic acid, and the solution, after being saturated with hydrogen chloride, is heated in a sealed tube at 100° , it yields phthalimide and ammonium chloride.

Orthocyanodiphenylmethane, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Ph}$, is obtained when orthocyanobenzyl chloride (10 grams) is boiled with benzene (50 c.c.) and aluminium chloride (10 grams) for 12 hours. It boils at $313\text{--}314^\circ$, melts at 19° , and is insoluble in light petroleum. When the compound is heated in a sealed tube at $170\text{--}180^\circ$ with hydrochloric acid (sp. gr. 1.19), orthobenzylbenzoic acid (m. p. 117°) is produced; whilst if heated in a sealed tube at 100° with a solution of hydrogen chloride in 75 per cent. acetic acid, *orthobenzylbenzamide*, $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$, is formed; this crystallises from alcohol in white needles, and melts at 163° . It also yields the *nitro-derivative*, $\text{CN}\cdot\text{C}_{13}\text{H}_{10}\cdot\text{NO}_2$, on treatment with fuming nitric acid, and when it is cautiously heated on the water-bath with concentrated sulphuric acid, a mixture of anthranol and anthraquinone is obtained.

Orthobenzylbenzylamine, $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}_2$, is produced in small quantity when a solution of orthocyanodiphenylmethane (10 grams) in alcohol (200 c.c.) is heated in a reflux apparatus with sodium (20 grams); the *hydrochloride* melts at 220° , and the *platino-chloride* at 197° . The *thiamide*, $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CS}\cdot\text{NH}_2$ is formed when a solution of the cyano-compound in alcoholic ammonia is

saturated with hydrogen sulphide, and heated at 100° in a sealed tube; it melts at 153° .

Orthocyanophenyltolylmethane, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Me}$, is obtained by heating together orthocyanobenzyl chloride, toluene, and aluminium chloride. It boils at $324\text{--}326^{\circ}$ (750 mm.) or at 296° (89 mm.), and, when heated at 100° with a saturated solution of hydrogen chloride in 75 per cent. acetic acid, yields the *amide*, $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Me}$, which crystallises from benzene in white leaflets, and melts at 123° .

Ethyl diorthocyanobenzylcyanacetate, $\text{CN}\cdot\text{C}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN})_2\cdot\text{COOEt}$, is obtained when a solution of orthocyanobenzyl chloride (15.1 grams) dissolved in alcohol (20 c.c.) is added to a mixture of ethyl cyanacetate (11.3 grams) and sodium (2.3 grams) dissolved in alcohol (40 c.c.). It separates from dilute alcohol in white, rhombic crystals, melts at $122\text{--}123^{\circ}$, and when heated on the water-bath with normal alcoholic potash yields the corresponding *acid*; this melts at 160° with evolution of carbonic anhydride and the formation of *diorthocyanobenzylacetoneitrile*, a compound which crystallises from dilute alcohol in tufts of needles, melts at 130° , and is insoluble in ether. Ethyl dibenzylcyanacetate is obtained in a similar manner from benzyl chloride and ethyl cyanacetate; on hydrolysis with alcoholic potash, it gives the *acid* $\text{CN}\cdot\text{C}(\text{CH}_2\text{Ph})_2\cdot\text{COOH}$, which separates from alcohol in granular crystals, and melts at $188\text{--}189^{\circ}$ with evolution of carbonic anhydride, and the formation of dibenzylacetoneitrile (Abstr., 1888, 705).

Orthonitrobenzyl thiocyanate, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{SCN}$, is prepared by heating a solution of orthonitrobenzyl chloride (25 grams) in alcohol (75 c.c.) with potassium thiocyanate (15 grams) for an hour on the water-bath; it is precipitated on adding water, separates from dilute alcohol in rhombic crystals, and melts at 75° ; it exerts an irritating effect on the mucous membrane. When an alcoholic solution is heated on the water-bath in a reflux apparatus with $3\frac{1}{2}$ times its weight of stannous chloride and hydrochloric acid (sp. gr. 1.19) for two hours, *orthamidobenzyl thiocyanate* is formed and can be isolated in the usual manner; it crystallises from hot water in almost colourless, thick needles, and melts at $137\text{--}138^{\circ}$. The *hydrochloride* forms silky needles, and melts at 212° ; the *platinochloride* melts at $215\text{--}217^{\circ}$; and the *picrate* melts at 223° with decomposition.

If orthonitrobenzyl thiocyanate is dissolved in alcoholic ammonia, and a current of hydrogen sulphide passed through the solution for two hours, a yellow compound insoluble in water and in acids is obtained; after crystallisation from alcohol, it melts at $112\text{--}113^{\circ}$, and is probably *orthonitrobenzyl bisulphide*, $\text{S}_2(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$. A compound having properties different from those of the substance last mentioned has been described as orthonitrobenzyl bisulphide by Jahoda (Abstr., 1890, 488), and the author suggests that the latter is perhaps the corresponding mercaptan $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SH}$. A. R. L.

Preparation of Optically Inactive Cymene from Oil of Caraway. By L. VOLPYAN (*Chem. Centr.*, 814—815; from *Pharm. Zeit. Russ.*, 31, 193—196, 211—216).—Optically inactive cymene has not previously been obtained from oil of caraway in a pure condition,

the samples prepared invariably containing some terpene, or consisting of a mixture of two cymenes. In order to prepare a pure hydrocarbon, oil of caraway was distilled, and the fraction coming over at 165—225° collected apart and treated with sodium hydrogen sulphite and potassium hydroxide in order to remove cuminaldehyde. The oil was again distilled, when each fraction of higher boiling point was found to be less dextrorotatory than the one obtained immediately before it. For example, the 160—163° fraction had a rotatory power $[\alpha]_D = +22^\circ 15'$, whilst the 174—176° fraction gave $[\alpha]_D = +3^\circ 36'$. The latter, which appeared to be the purest, was fractionated several times, and finally a distillate, boiling constantly at 174—176°, and having a rotatory power $[\alpha]_D = +2^\circ 36'$, was obtained. This product, on redistillation, showed no further lowering of the dextrorotatory power.

In order to separate the terpene, which in all probability gave the hydrocarbon its optical activity, a cymene, having the rotatory power $[\alpha]_D = +8^\circ 41'$, was carefully dehydrated with calcium chloride, saturated with hydrogen chloride at -18° , and fractionally distilled under a reduced pressure of 50 mm. The 103—106° fraction thus obtained was then distilled under ordinary pressure, when a hydrocarbon boiling constantly at 175—177°, and giving a rotation of $+1^\circ 17'$ in a 100 mm. tube, was obtained. On repeating the treatment with hydrogen chloride, a pure distillate was obtained, of the formula $C_{10}H_{14}$, which boiled constantly at 175—177°, and showed no rotatory power. The cymene prepared in this way is a clear, colourless liquid, having a pleasant odour quite distinct from that of *Ol. citri*. It boils constantly at 175—176.5°, and has a sp. gr. of 0.85957 at 15°, and 0.8585 at 20°. G. T. M.

Phenylacetylene Diiodide. By A. PERATONER (*Gazzetta*, 22, ii, 65—85).—The author has attempted to prepare stereoisomeric phenylacetylene diiodides, but with the same lack of success as in the case of acetylene diiodide (Abstr., 1891, 654).

A mixture of phenylacetylene (2 grams) and iodine (5 grams) dissolved in glacial acetic acid, alcohol, carbon bisulphide, or concentrated potassium iodide solution (100 c.c.) after a time deposits a product which, when decolorised by sulphurous anhydride and crystallised from alcohol (50 per cent.) or dilute acetic acid, is found to be *phenylacetylene diiodide*, $C_6H_5C\equiv CHI$. It crystallises in almost colourless laminae, melts at 76° , and gives off iodine at 150° ; the molecular weight, determined by the cryoscopic method in acetic acid solution, is normal. It soon turns red on exposure to light, and can be distilled in a current of steam. The same substance is obtained on heating a solution of phenylacetylene (2 grams), iodine (5 grams), and iodic acid (10 grams) in absolute alcohol (20 c.c.) for 20 hours.

On oxidising phenylacetylene diiodide with chromic acid mixture, benzoic acid is formed. When treated with zinc dust in cold alcoholic solution, no appreciable action occurs, but on boiling for three hours in a reflux apparatus, complete reduction to phenylacetylene takes place. On heating the diiodide (5 grams) with mercuric chloride (10 grams)

and water (30 grams) for two hours in a closed tube at $110-120^{\circ}$, and eliminating the unchanged phenylacetylene diiodide by distilling the product in a current of steam, an oil is obtained which, after two repetitions of the above treatment, boils at 222° , and agrees in properties with the phenylacetylene dichloride, $\text{CPhCl}:\text{CHCl}$, described by Dyckerhoff (Abstr., 1878, 327, 481). Phenylacetylene diiodide has of course a similar constitution.

The author has endeavoured to prepare an isomeric diiodide by heating diiodocinnamic acid in a sealed tube at 120° with dilute hydrochloric acid (1:12). The product contained free iodine, and on distilling it in a current of steam, a little acetophenone volatilised and a brown resin was left. This, after repeated precipitations from its solution in benzene by light petroleum and subsequent crystallisation from ether, yielded triphenylbenzene.

On heating diiodocinnamic acid (10 grams) with water (160 c.c.) in sealed tubes at 140° for four to five hours, iodine and carbonic anhydride are liberated, and a mixture of acetone with crystals of the triiodocinnamene prepared by Liebermann and Sachse (Abstr., 1892, 470) is obtained. On heating the tubes at 110° for two hours, however, a mixture of unaltered diiodocinnamic acid and the phenylacetylene diiodide described above is formed.

Action occurs when phenyliodacetylene, prepared by Liebermann and Sachse's method, is left in the cold for 24 hours in contact with concentrated hydriodic acid, or the mixture is heated for two hours on the water-bath. No product containing iodine could be isolated. On passing dry hydrogen iodide into a cooled solution of phenyliodacetylene (10 grams) in glacial acetic acid (100 c.c.) and leaving the product in sealed tubes for eight days, a satisfactory yield of the phenylacetylene diiodide described above is obtained. W. J. P.

Phenyliodacetylene. By A. PERATONER (*Gazzetta*, 22, ii, 94—99).—Phenyliodacetylene, $\text{CPh}:\text{CI}$, boils at $134-138^{\circ}$ under a pressure of 22 mm.; at 140° it becomes strongly coloured, and on cooling solidifies, owing to the formation of the diiodide. On treating it with hydrogen iodide in acetic acid solution, a product is obtained from which acetophenone is eliminated by distillation in a current of steam; the residue contains triphenylbenzene. It is slowly converted into a resin by exposure to sunlight. When shaken with aqueous alcoholic ammoniacal cuprous chloride solution in an atmosphere of hydrogen, a yellow precipitate is formed; this is collected, washed with water, and boiled with alcohol and ether. It has the composition $\text{CPh}:\text{C}:\text{Cu}$.

Phenyliodacetylene, when heated at 120° under 4 atmospheres pressure with zinc ethide and ether in an autoclave, yields a resinous product containing phenylethylacetylene. W. J. P.

Dinitrophenol [= 1:2:4]. By F. REVERDIN and C. DE LA HARPE (*Chem. Centr.*, 1892, ii, 40; from *Arch. Sci. phys. nat. Geneva*, [3], 27, 541—543).—400 grams of sulphuric acid, sp. gr. 1.82, is heated to 110° , 200 grams of phenol added, and the whole heated at $130-140^{\circ}$ for five hours. The product is then poured into 600 c.c.

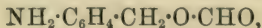
of water; 1375 grams of nitric acid, sp. gr. 1.2, is now added, the temperature not being allowed to exceed 40—50°, the whole is allowed to remain for 24 hours at the ordinary temperature, then heated from time to time on the water-bath during three days, and finally allowed to cool and filtered. The crystalline mass thus obtained is nearly pure dinitrophenol, and is rendered quite pure by twice boiling out with 2 litres of water. It melts at 114°, and, on reduction, yields the diamidophenol; this forms colouring matters when oxidised, or when its hydrochloride is heated with aromatic amines; the hydrochloride makes an indifferently good photographic developer.

C. F. B.

Orthonitrobenzyl Alcohol. By C. PAAL and A. BODEWIG (*Ber.*, 25, 2961—2966).—The best method of preparing orthonitrobenzyl alcohol, hitherto published, is that of Fischer, who obtained it by the action of alcoholic solutions of salts of organic acids on orthonitrobenzyl chloride and hydrolysis of the resulting salts. The reaction, however, is only quantitative when the mixture is heated in sealed tubes at 120°, which precludes the preparation of large quantities at once; if, however, the reaction is carried out in aqueous instead of alcoholic solution, it proceeds quantitatively at 100°, and the salts may, in this way, be readily prepared in any quantity.

Orthonitrobenzyl acetate, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OAc}$, is obtained from orthonitrobenzyl chloride and concentrated aqueous sodium acetate, and crystallises from light petroleum or dilute alcohol in flat, white needles melting at 35—36°, and almost insoluble in water; the *benzoate*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$, obtained in a similar manner from sodium benzoate, crystallises from dilute alcohol in concentric aggregates of white needles, melts at 94°, is very slightly soluble in light petroleum, and insoluble in water. To obtain orthonitrobenzyl alcohol, the acetate is hydrolysed with moderately dilute sulphuric acid, or the benzoate with alcoholic potash, the latter giving the best results; it crystallises in slightly yellowish needles, and melts at 71—74°. When boiled with formic acid, it yields the *formate*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{O}\cdot\text{CHO}$, which is an oil and could not be obtained pure.

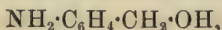
The formate, acetate, and benzoate are readily reduced by zinc dust and hydrochloric acid with formation of the corresponding salts of orthamidobenzyl, which, however, very readily undergo hydrolysis, yielding orthamidobenzyl alcohol. The *formate*,



is an unstable oil; the *acetate* crystallises in white needles; the *benzoate*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OBz}$, separates as an oil, which soon crystallises and yields a *hydrochloride*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OBz}\cdot\text{HCl}$, crystallising from alcoholic ether in colourless prisms and melting at 143°; it is soluble in alcohol, insoluble in ether, and is dissociated by water.

Acidyl derivatives of orthamidobenzyl alcohol have also been prepared by Söderbaum and Widman (*Abstr.*, 1889, 972), the acidyl group being in some cases combined with the nitrogen atom. These investigators endeavoured to convert the latter compounds into

derivatives of cumazone, $\text{C}_6\text{H}_4\text{<}\begin{matrix} \text{N}=\text{CH} \\ \text{CH}_2\cdot\text{O} \end{matrix}$ (Abstr., 1884, 302), but without success; the authors have made similar unsuccessful attempts to prepare cumazone derivatives from the acetate and benzoate; the formate yields, on distillation, water and an oil which soon partially crystallises; the crystals consist of *orthamidobenzyl alcohol*,



which, after recrystallisation from dilute alcohol, forms white plates melting at 82° . The examination of the basic oil is not yet completed, but it appears to consist chiefly of a cumazone derivative.

H. G. C.

Derivatives of Quinol, Resorcinol, and Phloroglucinol. By G. CIAMICIAN and P. SILBER (*Gazzetta*, 22, ii, 56—64).—On passing dry chlorine into a cooled solution of dimethylquinol (3 grams) in glacial acetic acid (10 c.c.), much hydrogen chloride is evolved, and the liquid soon solidifies with formation of a dichlorodimethylquinol, which separates from alcohol in colourless prisms melting at 134° . This substance is probably identical with that obtained by Habermann (Abstr., 1879, 728), although the descriptions differ somewhat.

On passing dry chlorine into a solution of dimethylquinol (1 part) in glacial acetic acid (3 parts) without cooling, a mixture of tetrachlorodimethylquinol and chloranil separates. The former separates from an alcoholic solution of the mixture in crystals melting at 164° , not at 153 — 154° as stated by Habermann (*loc. cit.*). The mother liquor contains a *trichlorodimethylquinol*, which is obtained in minute, white needles melting at 91° , and is probably identical with the substance melting at 79° described by Habermann; it is isomeric with the compound prepared by the authors from cotoïn (compare Bartolotti, Abstr., 1892, 1315).

A solution of resorcinol (50 grams), potash (50 grams), and methyl iodide (130 grams) in methyl alcohol (150 c.c.), when heated in a reflux apparatus under a pressure of 250 mm. on the water-bath, yields an oil which has the composition of a dimethylresorcinol, and boils at 214 — 215° as stated by Habermann. It contains, however, far less methoxyl than is required by theory. A similar product is obtained on attempting to prepare the substance by the method given by Habermann (*loc. cit.*). A true dimethylresorcinol has, therefore, not yet been prepared.

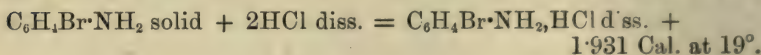
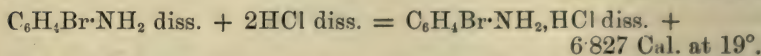
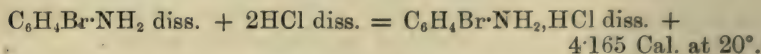
The authors have previously shown that trimethylbenzoylphloroglucinol, when fused with potash, yields benzoic acid and trimethylphloroglucinol. When monobromotrimethylbenzoylphloroglucinol (2 grams) is distilled with powdered potash (15 grams), an oil is obtained which soon solidifies; this consists of *bromotrimethylphloroglucinol*. It separates from dilute alcohol in feathery needles, and melts at 96 — 97° .

W. J. P.

Isomeric Monobromanilines. By A. NEMIROFFSKY (*J. Russ. Chem. Soc.*, 22, 482—488).—The author has carefully purified the

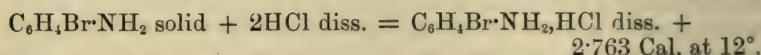
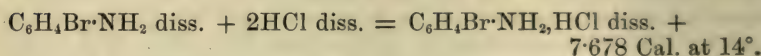
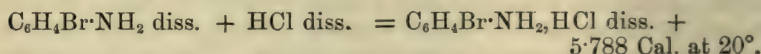
three isomeric monobromanilines, and made a comparative study of some of their properties.

Orthobromaniline crystallises in prisms melting at 29.6° . A litre of water at the ordinary temperature dissolves 2.169 grams.



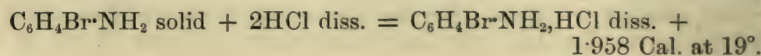
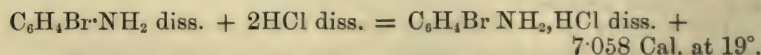
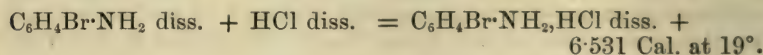
From the last two equations, it follows that the heat of dissolution of solid orthobromaniline is -4.896 Cal. at 19° . 0.8313 gram of the hydrochloride was dissolved in 100 c.c. water at 20° ; the heat of dissolution for this concentration and temperature was 4.160 Cal. When a solution of the hydrochloride (1 mol. in 2.5 litres water) is diluted repeatedly with 1 vol. of water, absorption of heat occurs on the first two dilutions amounting to -1.235 Cal. On further dilution, there is no appreciable absorption.

Metabromaniline forms needle-shaped crystals melting at 16.8° . At the ordinary temperature 1 litre of water dissolves 3.1928 grams.



The heat of dissolution of solid metabromaniline at 12° is thus -4.895 Cal. The heat of dissolution of the liquid at 20° is -2.090 Cal., from which it follows that the heat of fusion is about -2.8 Cal. 8.1003 grams of the hydrochloride when dissolved in 400 c.c. water absorbed -3.807 Cal. at 19° . No absorption was noted on dilution.

Parabromaniline melts at 62° . 2.160 grams dissolves at the ordinary temperature in 1 litre of water.



The heat of dissolution of the solid is, therefore, -5.1 Cal. at 19° .

10.1436 grams of the hydrochloride was dissolved in 400 c.c. water, the dissolution being accompanied by an absorption of 3.456 Cal. at 19° . Further dilution of the hydrochloride solution was not attended by absorption of heat.

From the thermochemical data given above, it would appear that the hydrochlorides of all the bromanilines are dissociated to a considerable extent into free base and hydrogen chloride when they are dissolved in water. J. W.

Action of Acetic Anhydride on Dimethylaniline. By F. REVERDIN and C. DE LA HARPE (*Bull. Soc. Chim.* [3], 7, 211—212).—When a mixture of acetic anhydride and dimethylaniline is exposed to the air, or, better, when air is blown through it, the liquid assumes a bluish tint, owing to the formation of tetramethyldiamidodiphenylmethane, of which as much as 10 per cent. may be obtained in a few days. Air is essential to the reaction, so that the strength of the standard solution of acetic anhydride in dimethylaniline used in the author's method of determining the relative amounts of aniline, methylaniline, and dimethylaniline in a mixture of those substances (Abstr., 1889, 1038) does not change if the solution is kept in full, well stoppered bottles. JN. W.

Orthamidobenzyl Alcohol and its Derivatives. By C. PAAL and E. LAUDENHEIMER (*Ber.*, 25, 2967—2973).—Friedländer and Henriques (Abstr., 1883, 187) have shown that orthamidobenzyl alcohol may be readily prepared by the reduction of orthonitrobenzyl alcohol with zinc dust and hydrochloric acid in alcoholic solution, and as the nitrobenzyl alcohol can now be obtained in quantity (see p. 20), the authors have investigated the properties of the amido-compound and its derivatives.

Orthamidobenzyl alcohol, when recrystallised, may be distilled with very slight decomposition at 270—280°, whilst under 5—10 mm. pressure, it distils unchanged at 160°; the impure compound, however, decomposes on heating. The *hydrochloride*, $C_7H_9NO \cdot HCl$, forms white tablets melting at 108°, and readily soluble in alcohol; the *sulphate*, $(C_7H_9NO)_2H_2SO_4$, is a crystalline powder melting at 114°. It combines with almost all aldehydes with elimination of water, forming derivatives of the type $OH \cdot CH_2 \cdot C_6H_4 \cdot N \cdot CHR$, which are for the most part crystalline compounds, stable towards alkalis, but resolved into their components by mineral acids. With the exception of acetone, no ketone reacts readily with the amido-alcohol even in presence of a dehydrating agent.

Ethylidene-orthamidobenzyl alcohol, $CHMe \cdot N \cdot C_6H_4 \cdot CH_2 \cdot OH$, is obtained by the action of acetaldehyde on the amido-alcohol, and forms an oil which distils at 135—137° under a pressure of 5 mm.; *trichloroethylidene-orthamidobenzyl alcohol*, $CCl_3 \cdot CH \cdot N \cdot C_6H_4 \cdot CH_2 \cdot OH$, prepared in a similar manner from chloral, crystallises from dilute alcohol in white, lustrous plates melting at 92°. An *allylidene* derivative, $CH_2 \cdot CH \cdot CH(NH \cdot C_6H_4 \cdot CH_2 \cdot OH)_2$, is prepared by the action of acetaldehyde on amidobenzyl alcohol in alcoholic solution; it is an amorphous, reddish powder; the authors give this formula with reserve, although the analytical figures are in accord with it. The *benzylidene* derivative, $CHPh \cdot N \cdot C_6H_4 \cdot CH_2 \cdot OH$, forms white plates which are insoluble in water, and melts at 115°. The *metanitrobenzylidene*, *ortho**hydroxybenzylidene*, and *para**hydroxybenzylidene* derivatives all form yellowish

needles, and melt at 93° , 117° , and 137° respectively. The *vanillidine* derivative, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$, crystallises from alcohol in hemispherical aggregates of white needles, melts at 119° , and is extremely susceptible to the action of mineral acids; the *piperonidine* derivative, $\text{CH}_2\langle\text{O}\rangle\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$, forms stellate groups of white needles melting at 78° , and the *isopropylbenzylidine* derivative, $\text{C}_6\text{H}_4\text{Pr}^{\beta}\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$, white plates melting at 103° .

Acetone, as already mentioned, combines very readily with orthamidobenzyl alcohol, and yields *isopropylene-orthamidobenzyl alcohol*, $\text{CMe}_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$, which crystallises in large plates or flat needles, and melts at 120° . In small quantities, it distils at a high temperature unchanged, and, like the compounds obtained from the aldehydes, is stable towards alkalis, but is resolved into its components by mineral acids. H. G. C.

Methylphenylmercurammonium Hydroxide and Salts. By L. PESCI (*Gazzetta*, 22, ii, 32—36).—*Methylphenylmercurammonium acetate*, $\text{NMePhHg}\cdot\text{OAc}$, is obtained by adding a dilute alcoholic solution of methylaniline (2 mols.) to a concentrated alcoholic (50 per cent.) solution of mercuric acetate (1 mol.). The salt separates in brilliant, transparent laminæ, and is recrystallised from alcohol. It melts with decomposition at 149° , and is soluble in cold alcohol and acetic acid, but insoluble in ether and cold water. It is decomposed on boiling with water. On suspending it in water and adding potash, it yields the *hydroxide*, $\text{NMePhHg}\cdot\text{OH}\cdot\text{H}_2\text{O}$, as colourless laminæ of pearly lustre, which lose their water of crystallisation over sulphuric acid. This substance melts at 118° and decomposes at 120° . It has an alkaline reaction and a caustic taste, is soluble in alcohol, sparingly so in cold water and insoluble in ether. It is decomposed by boiling with water, and on treatment with hydrogen sulphide, yields mercuric sulphide and salts of methylaniline. The *chloride* forms an amorphous, yellow powder, which, on exposure to light, turns green. It is insoluble in water and alcohol, decomposes at 108° , and has similar properties to the *bromide*, which decomposes at 120° yielding a violet product. The *nitrate* is obtained by the action of dilute nitric acid on the hydroxide; it forms colourless, hexagonal laminæ, and is very soluble in water, giving a solution which soon decomposes, and turns blue on heating; it is decomposed by alcohol and becomes green when kept. It decomposes at 150° , giving a brown product. The *hydrogen sulphate* is obtained in microscopic, transparent prisms, containing 1 mol. H_2O ; it decomposes at 130° and is slowly converted into a greenish substance by the action of light. W. J. P.

Action of Carbonyl Chloride on Sodiophenylhydrazine. By A. PERATONER and G. SIRINGO (*Gazzetta*, 22, ii, 99—105).—A diphenylurazine isomeric with that prepared by Pinner (*Ber.*, 21, 2330) and Heller (*Abstr.*, 1891, 1213) is obtained by the gradual addition of carbonyl chloride (15 grams) dissolved in benzene (45 grams) to sodiophenylhydrazine (40 grams) suspended in benzene

(150 grams). Heat is developed, and after 12 hours the liquid is filtered and the residue washed first with benzene and then with water. The urazine (10 grams) is repeatedly precipitated, first from its solution in glacial acetic acid by water, and finally from its chloroform solution by light petroleum; it forms white flocks, melts at 148–150°, and gives a normal molecular weight by the cryoscopic method in acetic acid solution. It is very soluble in alcohol and chloroform, sparingly so in benzene and insoluble in water, ether, and light petroleum. On heating with acetic anhydride, it yields a *mon-acetyl* derivative as an amorphous, yellow powder which gives a normal molecular weight by the cryoscopic method.

The diphenylurazine described above is not identical with that obtained by Pinner (*loc. cit.*); the constitution of the latter not being known, it is impossible to say which of them is the symmetrical and which the unsymmetrical isomeride.

W. J. P.

Action of Carbon Bisulphide on Orthamidobenzyl Alcohol.

By C. PAAL and E. LAUDENHEIMER (*Ber.*, 25, 2978–2980).—When carbon bisulphide is boiled with orthamidobenzyl alcohol in alcoholic solution, a reaction takes place similar to that occurring between carbon bisulphide and orthamidophenol. Whether the product has the

formula $C_6H_4 \begin{smallmatrix} NH \cdot CS \\ | \\ CH_2 \cdot O \end{smallmatrix}$, or the tautomeric formula $C_6H_4 \begin{smallmatrix} N = C \cdot SH \\ | \\ CH_2 \cdot O \end{smallmatrix}$,

has not yet been decided. The authors propose to term the substance *thiocumazone*, thus showing its connection with Widman's cumazonic acids (*Abstr.*, 1884, 303).

Thiocumazone crystallises from dilute alcohol in white needles which are soluble in hot water and organic solvents and also in mineral acids and alkalis; it melts at 142° with evolution of hydrogen sulphide. The *platinchloride* forms yellow, amorphous flakes, and is insoluble in water and alcohol; the *potassium* salt, C_8H_6NSOK , crystallises in white plates having a satiny lustre, and deliquesces in the air.

H. G. C.

Diphenylanilguanidine. By W. MARCKWALD and P. WOLFF (*Ber.*, 25, 3116–3119).—Diphenylanilguanidine, $NHPh \cdot N:C(NHPh)_2$, or $NHPh \cdot C(NPh) \cdot NH \cdot NHPh$, is formed when either of the isomeric diphenylthiosemicarbazides (compare next abstract) is boiled with aniline (1 mol.) in alcoholic solution in presence of lead oxide; it is a colourless, crystalline powder, melts at 160°, turns reddish on exposure to the air, and is moderately easily soluble in benzene and toluene, but only sparingly in alcohol and ether. It is identical with the compound first obtained by L. Marckwald (*Inaug. Diss.*, Berlin, 1888) by the action of lead oxide on an alcoholic solution of diphenylthiocarbamide and phenylhydrazine, and also with that obtained by Wessel (*Abstr.*, 1888, 1083) by heating phenylhydrazine with carbodiphenylimide; the melting point (138–139°) given by Marckwald is much too low, whereas that given by Wessel is about 44° too high. The *platinchloride*, $(C_{19}H_{18}N_4)_2 \cdot H_2PtCl_6$, is a yellowish-green compound, readily soluble in alcohol. The *picrate*, $C_{19}H_{18}N_4 \cdot C_6H_3N_3O_7$, crystallises in yellow needles, melts at 183° with decomposition, and

is readily soluble in alcohol, ether, and acetone, but only sparingly in benzene and toluene, and insoluble in water.

The *azo*-compound, $\text{NHPh}\cdot\text{C}(\text{NPh})\cdot\text{N}_2\text{Ph}$, is obtained when an alcoholic solution of diphenylanilguanidine is boiled with precipitated mercuric oxide; it crystallises from dilute alcohol in lustrous, bright-red needles, melts at 111° , and is soluble in acids and most ordinary solvents, but insoluble in water.

A compound of the composition $\text{C}_{32}\text{H}_{28}\text{N}_6$ is formed with liberation of ammonia, benzene, and phenylhydrazine, when diphenylanilguanidine is heated at a moderately high temperature; it separates from boiling alcohol in the form of a colourless, crystalline powder, melts at 201° , and is only very sparingly soluble in all ordinary solvents. It is identical with the compound obtained by Wessel (*loc. cit.*) by heating diphenylanilguanidine with carbodiphenylimide. The *picate*, $\text{C}_{32}\text{H}_{28}\text{N}_6\cdot\text{C}_6\text{H}_5\text{N}_3\text{O}_7$, is a yellow, crystalline powder, melting at 240° with decomposition.
F. S. K.

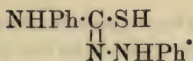
Stereoisomeric Thiosemicarbazides. By W. MARCKWALD (*Ber.*, 25, 3098—3115; compare Dixon, *Trans.*, 1892, 1012).—All the thiosemicarbazides which have been investigated, and which have been formed by the combination of fatty or aromatic thiocarbimides with phenylhydrazine, or with paratolylhydrazine, exist in two forms; the α -modification is less stable and melts at a lower temperature than the β -modification, into which it is converted when heated at a moderately high temperature, or when treated with hydrochloric acid. The behaviour of the two diphenylthiosemicarbazides is fully described below, and may be taken as correctly representing that of the other semicarbazides which show the same kind of isomerism.

Various thiocarbamides were examined, but were found to exist in only one form; symmetrical phenylparatolylthiocarbamide, for example, melts at 142° , whether prepared by the combination of paratolylthiocarbimide and aniline or by the combination of paratoluidine and phenylthiocarbimide. A number of thiosemicarbazides, prepared from asymmetrical substituted phenylhydrazines, were also examined, but in no case was the existence of two modifications observed.

The α - and β -modifications of the thiosemicarbazides are isomeric, as was proved, in the case of methylphenylthiosemicarbazide by molecular weight determinations in glacial acetic acid solution; they are, moreover, chemically, and not purely physically, isomeric, since, as is shown in the case of the diphenylthiosemicarbazides, they yield different additive products with methyl iodide. From the readiness with which the α -modifications of the thiosemicarbazides are converted into the corresponding β -forms, from the behaviour of the two diphenylthiosemicarbazides with methyl iodide, and with aniline and lead oxide (compare preceding abstract), and more especially from the study of the products obtained by treating the two diphenylthiosemicarbazides with carbonyl chloride, the author concludes that the two modifications are stereochemically isomeric; α -diphenylthiosemicarbazide may, therefore, be represented by the anti-configuration

$$\begin{array}{c} \text{SH}\cdot\text{C}\cdot\text{NHPh} \\ \parallel \\ \text{N}\cdot\text{NHPh} \end{array}$$

the β -modification by the syn-configuration



α -Diphenylthiosemicarbazide, prepared by treating phenylthiocarbimide with phenylhydrazine in well-cooled alcoholic solution, is only sparingly soluble in cold alcohol and benzene, but more readily in the hot solvents and in hot acetone. When heated in a capillary tube in the ordinary manner, it sinters at 139° , but does not melt until the temperature has risen to 176° ; if, however, it is immediately heated at 139° , it liquefies completely, solidifies again a few seconds later, and then melts at 176° , having been converted into the β -modification; the true melting point of the α -modification is, therefore, 139° . Even after recrystallisation from solvents, it shows this peculiar behaviour on heating, but, after having once been liquefied, it shows no signs of melting until the temperature rises to 176° ; it also crystallises unchanged from hot potash, but, on prolonged boiling with alcoholic potash, it is partially converted into the β -modification; on adding a trace of hydrochloric acid to its boiling alcoholic solution, it is completely converted into the isomeride.

β -Diphenylthiosemicarbazide is more sparingly soluble than the α -modification in all ordinary solvents, and melts at 176° ; it crystallises from its solutions unchanged, and cannot be converted into the α -modification.

α -Phenylparatolylthiosemicarbazide, $\text{C}_7\text{H}_7\text{NH} \cdot \text{C}(\text{SH}) \cdot \text{N}_2\text{HPh}$, prepared from paratolylthiocarbimide and phenylhydrazine in like manner, sinters at about 150° , being converted into the β -modification; it is only sparingly soluble in cold alcohol, acetone, and benzene, but more readily in the hot solvents. The β -modification melts at 176° , and is very sparingly soluble in benzene and only sparingly in hot acetone and alcohol.

α -Paratolylphenylthiosemicarbazide, $\text{NHP} \cdot \text{C}(\text{SH}) \cdot \text{N}_2\text{H} \cdot \text{C}_7\text{H}_7$, prepared from phenylthiocarbimide and paratolylhydrazine, melts at 123° , being converted into the β -modification; it is only sparingly soluble in cold, but readily in hot alcohol. The β -modification melts at 175° , and is more sparingly soluble than the isomeride.

α -Phenylmethylthiosemicarbazide, $\text{NHMe} \cdot \text{C}(\text{SH}) \cdot \text{N}_2\text{HPh}$, obtained by the combination of methylthiocarbimide and phenylhydrazine (compare Dixon, Trans., 1890, 261), melts at 90 – 91° , is very readily soluble in cold acetone and glacial acetic acid, and moderately easily in cold alcohol and chloroform, but only sparingly in hot water; it is converted into the β -modification when heated at about 130° . The β -modification melts at 163 – 164° , and is readily soluble in cold acetone and glacial acetic acid, but more sparingly in alcohol and benzene.

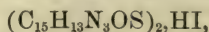
A compound of the composition $\text{C}_{14}\text{H}_{16}\text{N}_3\text{SI}$ is formed when α -diphenylthiosemicarbazide is treated with methyl iodide in hot acetone solution; it crystallises from alcohol in colourless needles, melts at 164° , and is readily soluble in acetone and hot alcohol, but only very sparingly in benzene. The isomeride, $\text{C}_{14}\text{H}_{16}\text{N}_3\text{SI}$, obtained from β -diphenylthiosemicarbazide in like manner, forms colourless crystals, melts at 245° , and is more sparingly soluble than the α -compound.

When β -diphenylthiosemicarbazide is treated with carbonyl chloride in toluene solution, it is converted into the phenylanilidothiobiazolone described by Freund (Abstr., 1892, 508; 1890, 1440; 1888, 1187); this compound, contrary to Freund's statement, is not decomposed by an alkaline lead solution.

Phenylanilidothiobiazolone is also formed, together with an approximately equal quantity of diphenylimidobiazolonyl- μ -mercaptide, when α -diphenylthiosemicarbazide is gradually added to excess of a well-cooled toluene solution of carbonyl chloride; the two products can be separated by treatment with ammonia, in which phenylanilidothiobiazolone is insoluble.

Diphenylimidobiazolonyl- μ -mercaptide, $\begin{array}{c} \text{C(SH)·NPh} \\ \parallel \\ \text{N} \text{---} \text{NPh} \end{array} > \text{CO}$, is precipitated in crystals on acidifying the ammoniacal extract; it separates from hot alcohol in colourless crystals, melts at 219—221°, and is very readily soluble in hot alcohol and glacial acetic acid, but only sparingly in cold alcohol, ether, benzene, and chloroform, and insoluble in water. Molecular weight determinations gave results agreeing with those required for the molecular formula given above. It has a distinctly acid character, and its solution in ammonia gives, with many salts of the heavy metals, insoluble compounds, which are stable towards dilute mineral acids; lead acetate, for example, yields a light-yellow, crystalline compound, copper sulphate a dirty-green, amorphous precipitate, and silver nitrate a colourless, amorphous compound of the composition $\text{C}_{14}\text{H}_{10}\text{N}_3\text{OSAg}$.

Diphenylimidobiazolonyl- μ -methyl sulphide hydriodide,



is slowly deposited in yellowish crystals when the preceding compound is treated with methyl iodide in alcoholic or chloroform solution at the ordinary temperature; it melts at 155—156°, and is very readily soluble in hot water, but only sparingly in alcohol and cold water, and very sparingly in ether and chloroform. The *base*, $\text{C}_{15}\text{H}_{13}\text{N}_3\text{OS}$, prepared by decomposing an aqueous solution of the salt with concentrated potassium carbonate, crystallises from hot water, melts at 185°, and is very readily soluble in hot water, cold alcohol, ether, chloroform, and glacial acetic acid; its molecular weight was determined in glacial acetic acid and in benzene solutions, with results which showed that it has the molecular formula given above; it is decomposed by hot alkalis with liberation of methyl mercaptan. The *platinochloride*, $(\text{C}_{15}\text{H}_{13}\text{N}_3\text{OS})_4, \text{H}_2\text{PtCl}_6$, crystallises from hot water in orange-red prisms, melts at 186° with decomposition, and is only sparingly soluble in cold water and alcohol, but moderately easily in the hot solvents.

Diphenylimidobiazolone, $\begin{array}{c} \text{CH·NPh} \\ \parallel \\ \text{N} \text{---} \text{NPh} \end{array} > \text{CO}$, is produced when diphenylimidobiazolonyl- μ -mercaptide is oxidised with the theoretical quantity of hydrogen peroxide in sodium carbonate solution; it crystallises from alcohol in colourless needles, melts at 249°, and is very readily soluble in cold glacial acetic acid, but only very sparingly in ether,

benzene, and alcohol, and insoluble in water and sodium carbonate; it crystallises unchanged from dilute mineral acids, and is not decomposed by boiling alkalis. Molecular weight determinations gave results in accordance with those required by a compound of the molecular formula given above.

Triphenylthiosemicarbazide, $\text{NHPH}\cdot\text{CS}\cdot\text{NH}\cdot\text{NPh}_2$, is formed when asymmetrical diphenylhydrazine is treated with phenylthiocarbimide in alcoholic solution; it melts at 181° , decomposes at a higher temperature, and is readily soluble in hot glacial acetic acid, but only sparingly in ether, alcohol, and cold glacial acetic acid.

Diphenylmethylthiosemicarbazide, $\text{NHMe}\cdot\text{CS}\cdot\text{NH}\cdot\text{NPh}_2$, prepared from methylthiocarbimide and asymmetrical diphenylhydrazine, melts at $203\text{--}204^\circ$, and is only sparingly soluble in ether, cold alcohol, and glacial acetic acid, but moderately easily in hot alcohol and hot glacial acetic acid.

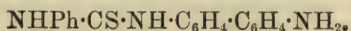
Diphenylallylthiosemicarbazide melts at 108° , not at 103° , as stated by Michaelis and Claesson (Abstr., 18'9, 1161).

Diphenylmethylthiosemicarbazide, $\text{NHPH}\cdot\text{CS}\cdot\text{NH}\cdot\text{NMePh}$, prepared from phenylthiocarbimide and asymmetrical methylphenylhydrazine, melts at 154° , as stated by Fischer.

Dimethylphenylthiosemicarbazide, $\text{NHMe}\cdot\text{CS}\cdot\text{NH}\cdot\text{NMePh}$, obtained by the combination of methylthiocarbimide and asymmetrical methylphenylhydrazine, crystallises in lustrous plates, melts at $162\cdot5^\circ$, and is very readily soluble in hot alcohol, benzene, and glacial acetic acid, but only sparingly in cold ether.

Diphenylmethylthiosemicarbazide, $\text{NHPH}\cdot\text{CS}\cdot\text{NMe}\cdot\text{NHPH}$, is readily obtained by treating phenylthiocarbimide with symmetrical methylphenylhydrazine in alcoholic solution; it crystallises in colourless needles, melts at 175° , and is only sparingly soluble in cold alcohol and ether, but very readily in hot alcohol and benzene.

Triphenylthiosemicarbazide, $\text{NHPH}\cdot\text{CS}\cdot\text{NPh}\cdot\text{NHPH}$, is formed when hydrazobenzene is boiled for a long time with phenylthiocarbimide in alcoholic solution; it melts at $173\text{--}174^\circ$, and dissolves freely in boiling benzene, toluene, and glacial acetic acid, but is only sparingly soluble in hot alcohol and ether; it does not combine with phenylthiocarbimide in boiling alcoholic solution, a fact which proves that it cannot be a benzidine derivative of the constitution



F. S. K.

Dibenzamide and Tribenzamide. By M. JAFFÉ (*Ber.*, 25, 3120—3121).—In the preparation of benzamide by the action of ammonium carbonate on benzoic chloride, small quantities of dibenzamide and tribenzamide are formed, and remain undissolved on treating the product with boiling water; on recrystallising the residue from hot alcohol, tribenzamide is deposited in slender, colourless needles melting at $201\text{--}202^\circ$ (corr.), and identical with the compound described by Curtius (Abstr., 1891, 58); the alcoholic mother liquors yield, on evaporation, a small quantity of dibenzamide, which, after recrystallisation from hot water, is obtained in colourless needles melting at 147° . The sum of the weights of the dibenzamide

and tribenzamide never exceeds 5 per cent. of the benzoic chloride employed, even when the method of preparation is altered; it is also immaterial whether commercial benzoic chloride, or a sample prepared from pure benzoic acid, is employed. F. S. K.

Seleno- and Thio. derivatives of Ethylamine. By W. MICHELS (*Ber.*, 25, 3048—3055).—Dibenzamidodimethyl diselenide does not react with phosphoric chloride in an analogous manner to the bisulphide (*Abstr.*, 1891, 817), but gives rise to μ -phenyloxazoline.

μ -Methylselenazoline, $\begin{matrix} \text{CH}_2\cdot\text{Se} \\ | \\ \text{CH}_2\cdot\text{N} \end{matrix} \gg \text{CMe}$, is obtained by heating a mixture of diamidodiethyl diselenide hydrochloride (1.6 grams), sodium acetate (0.9 gram), and acetic anhydride (3.9 grams) on the water-bath in a reflux apparatus for half an hour, adding phosphoric chloride (3.2 grams), and continuing the heating for a quarter of an hour. The product is rendered alkaline and distilled with steam; on adding alkali to the distillate, an oil separates which is extracted with ether. It boils at 160—162° (752.2 mm.), has a specific gravity above 1.5, and an index of refraction $n_D = 1.556$ at 20°. The *picrate* melts at 158—159°.

Phthalimidoethylbenzyl sulphide, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{CH}_2\text{Ph}$, is formed when ethylmercaptophthalimide (Gabriel, *Abstr.*, 1891, 815) is dissolved in absolute alcohol (2 parts), and an alcoholic solution of sodium ethoxide (1 mol.), and subsequently benzyl chloride, are gradually added with cooling; on pouring the product into water, the compound is precipitated; it crystallises from methyl alcohol in white leaflets, and melts at 76—78°. When it is dissolved in 10 per cent. potash, and hydrochloric acid added to the solution, *benzylthioethylphthalamic acid*, $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, separates; and this, on being heated in a reflux apparatus with concentrated hydrochloric acid (100 parts), yields phthalic acid and benzylthioethylamine hydrochloride. The *base* of the last-named salt, $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{NH}_2$, is a colourless oil of an unpleasant odour and a biting taste, boils at 270—272° (754.5 mm.), is very unstable, and absorbs carbonic anhydride from the air. The *picrate* melts at 125—127°; the *platinochloride* is a pale yellow, crystalline powder. The *benzoyl* derivative melts at 78—80°; when heated on the water-bath with phosphoric chloride, benzyl chloride passes over, and the residue, on being rendered alkaline and distilled in a current of steam, yields μ -phenylthiazoline. When an alcoholic solution of phthalimidoethylbenzyl sulphide is gently warmed with bromine water, the *sulphoxide*, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{C}_2\text{H}_4\cdot\text{SO}\cdot\text{CH}_2\text{Ph}$, which melts at 143—145°, separates in lustrous, white tables; whilst if the sulphide (3 mols.) is dissolved in 80 per cent. acetic acid, and warmed with a solution of chromic acid (4 mols.) in dilute acetic acid, the *sulphone*, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{C}_2\text{H}_4\cdot\text{SO}_2\cdot\text{CH}_2\text{Ph}$, is obtained; this crystallises from alcohol in white leaflets, melts at 137—139°, and decomposes into phthalic acid and benzyl chloride when heated in a sealed tube at 160°.

Phthalimidoethylbenzomercaptal, $\text{CHPh}(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{N}\cdot\text{C}_8\text{H}_4\text{O}_2)_2$, produced by heating phthalimidoethyl mercaptan with an excess of benz-

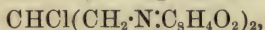
aldehyde in a current of hydrogen chloride at 100° , forms small prisms, melts at $155\text{--}156^{\circ}$, and is sparingly soluble in alcohol, but more readily in glacial acetic acid. When heated with 10 per cent. alkali, the phthalamic acid is precipitated on adding dilute acid to the solution; the precipitate, if heated in a reflux apparatus for two hours with 25 per cent. hydrochloric acid, yields phthalic acid and *amidoethylbenz-mercaptan hydrochloride*, $\text{CHPh}(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{NH}_2)_2\cdot 2\text{HCl}$, melting at 195° .

Acetone phthalimidoethylmercaptan, $\text{CMe}_2(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{N}\cdot\text{C}_8\text{H}_4\text{O}_2)_2$, obtained from phthalimidoethyl mercaptan and acetone, crystallises in small tablets, melts at $141\text{--}143^{\circ}$, and, when heated with hydrochloric acid, yields acetone, phthalic acid, and amidomercaptan.

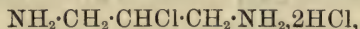
Phthalimidoethylformomercaptan, $\text{CH}_2(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{N}\cdot\text{C}_8\text{H}_4\text{O}_2)_2$, is formed by heating on the water-bath phthalimidoethyl mercaptan (10 grams), dissolved in absolute alcohol (20 c.c.), with a 5 per cent. solution of sodium ethoxide (22 c.c.) and methylene chloride (4 grams). It separates from glacial acetic acid in small, colourless crystals, melts at $133\text{--}134^{\circ}$, and, when heated with fuming hydrochloric acid (10 parts) at 180° , yields phthalic acid and *amidoethylformomercaptan hydrochloride*, $\text{CH}_2(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{NH}_2)_2\cdot 2\text{HCl}$, melting at $186\text{--}187^{\circ}$; the free base of the last-named salt is fairly soluble in water, and the *picrate* melts at $139\text{--}141^{\circ}$.

A. R. L.

Triamidopropane. By S. GABRIEL and W. MICHELS (*Ber.*, 25, 3056—3058).— β -Chlorotrimethylenedipthalimide,



is obtained by adding phosphoric chloride (7 grams) to finely pulverised β -hydroxytrimethylenedipthalimide (10 grams) suspended in boiling benzene (50 c.c.), and heating the mixture for a quarter of an hour; the compound is then collected and washed with benzene and aqueous alcohol. When crystallised from 70 per cent. acetic acid, it forms slightly-coloured, thick prisms, and melts at $208\text{--}209^{\circ}$. If it is heated in a sealed tube with fuming hydrochloric acid (10 parts) at $180\text{--}200^{\circ}$ for four hours, and the eliminated phthalic acid filtered off, the filtrate, on evaporation to dryness, yields a residue of β -chlorotrimethylenediamine hydrochloride,



which crystallises from alcohol in lustrous, white leaflets, and melts at 216° ; the *picrate* melts at 214° ; and the free base, which is very soluble in water, is precipitated from solutions of its salts by concentrated alkalis as a colourless oil.

Triphthalimidopropane, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{CH}(\text{CH}_2\cdot\text{N}\cdot\text{C}_8\text{H}_4\text{O}_2)_2$, is formed by heating an intimate mixture of potassium phthalimide (1 part) and β -chlorotrimethylenedipthalimide (2 parts) at $215\text{--}225^{\circ}$. The pulverised product is digested with 5 per cent. sodium hydroxide for half an hour, collected, and washed with water. The compound crystallises from glacial acetic acid in reddish needles, and melts at $226\text{--}227^{\circ}$. On heating it with hydrochloric acid at 100° , phthalic acid, ammonia, and a substance having the odour of pyridine were recognised, but apparently the expected triamidopropane was not present.

A. R. L.

Mesitylene. By S. LANDAU (*Ber.*, 25, 3011—3018).—*ω*-Mesitylphthalimide, $C_6H_3Me_2 \cdot CH_2 \cdot N : C_6H_4O_2$, is obtained by heating a mixture of equal weights of mesityl bromide, $C_6H_3Me_2 \cdot CH_2Br$, and potassium phthalimide at 220° for half an hour and then at 235° for two hours. The product is powdered, extracted with water, then with dilute sodium hydroxide, and crystallised from acetic acid. It forms white needles, melts at 157° , and is easily soluble in alcohol and hot acetic acid, more sparingly in ether, benzene, and chloroform.

ω-Mesitylphthalamide, $C_6H_3Me_2 \cdot CH_2 \cdot NH \cdot CO \cdot C_6H_4 \cdot COOH$, is obtained by warming the preceding compound on the water-bath with 10 per cent. potassium hydroxide until it dissolves, and then precipitating with hydrochloric acid. It crystallises from dilute alcohol or benzene in slender needles, melts at 152° , is insoluble in hot water, and easily soluble in alcohol and acetic acid, more sparingly in benzene. The *silver salt* is a white, crystalline precipitate, and decomposes above 182° . The acid is only very slightly decomposed by boiling with concentrated hydrochloric acid in a reflux apparatus for three hours.

ω-Mesitylamine, $C_6H_3Me_2 \cdot CH_2 \cdot NH_2$, is obtained by heating mesitylphthalimide with concentrated hydrochloric acid (5 parts) in a sealed tube at 190 — 200° for six hours. It is a colourless liquid, has a strong odour of herring brine, boils at 217 — 218° under 756 mm. pressure without decomposition, and eagerly absorbs carbonic anhydride from the air. The *hydrochloride* crystallises in four-sided prisms, and melts at 224° . The *nitrate* crystallises in long, white needles. The *picrate* forms yellow, rhombic crystals, and melts at 225° with decomposition. The *platinochloride* crystallises in golden-yellow, six-sided leaflets, and melts at 204° . The *acetyl compound* crystallises from dilute alcohol and acetic acid in needles, and melts at 78° . The *benzoyl compound* crystallises from alcohol in aggregates of white needles, melts at 78° , and is easily soluble in alcohol, benzene, and acetic acid.

ω-Mesitylcarbamide, $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot C_6H_3Me_2$, is obtained by warming an aqueous solution of mesitylamine hydrochloride with potassium cyanate. It crystallises from alcohol in silvery leaflets, and melts at 181° .

ω-Mesitylthiocarbamide, $NH_2 \cdot CS \cdot NH \cdot CH_2 \cdot C_6H_3Me_2$, is obtained by warming an aqueous solution of mesitylamine hydrochloride and potassium thiocyanate on the water-bath. It crystallises from water in slender, white needles, turns yellow on exposure to air, melts at 135° , and is easily soluble in alcohol and acetic acid.

Dimesitylthiocarbamide, $CS(NH \cdot CH_2 \cdot C_6H_3Me_2)_2$, is obtained by adding a slight excess of carbon bisulphide to an alcoholic solution of mesitylamine; it crystallises from alcohol in long, thin needles, and melts at 165° .

Allylmesitylthiocarbamide, obtained by gradually adding allylthiocarbimide to mesitylamine, crystallises from alcohol in white needles, melts at 91° , and is sparingly soluble in water, easily so in alcohol.

Dinitromesitylacetamide, $C_6HMe_2(NO_2)_2 \cdot CH_2 \cdot NHAc$, is obtained by

gradually adding mesitylacetamide to 4—5 times the quantity of fuming nitric acid cooled with ice. It crystallises from dilute alcohol in long, thin, pale yellow prisms, melts at 162° , and is easily soluble in alcohol, acetic acid, and mineral acids, sparingly in cold water.

Dinitromesitylamine is obtained by heating the preceding acetyl compound with hydrochloric acid in a sealed tube at 150° , and is a brown, odourless liquid which easily decomposes. The *hydrochloride* crystallises in leaflets, melts at 245° with decomposition, and is easily soluble in water, sparingly so in concentrated hydrochloric acid and absolute alcohol. The *picrate* crystallises from water in long, bright yellow prisms, decomposes at 220° , and is insoluble in alcohol. The *platinochloride* crystallises from water in golden-yellow leaflets.

ω_2 -*Diphthalimidomesitylene*, $C_6H_3Me(CH_2 \cdot N : C_6H_4O_2)_2$, is obtained by heating a mixture of dibromo- or dichloro-mesitylene with potassium phthalimide (2 mols.) at 220 — 240° for about half an hour. The product is crystallised from nitrobenzene, and dried on porous plates. It crystallises from acetic acid in brownish needles, melts at 244° , and is insoluble in alcohol.

Mesitylenediphthalamie acid, $C_6H_3Me \cdot (CH_2 \cdot NH \cdot CO \cdot C_6H_4 \cdot COOH)_2$, is obtained by boiling the preceding compound with alcoholic potash until it dissolves. It separates in white prisms on adding hydrochloric acid to the dilute ammoniacal solution, melts at 187° , and is easily soluble in alcohol and acetic acid, sparingly so in water.

ω_2 -*Diamidomesitylene*, $C_6H_3Me(CH_2 \cdot NH_2)_2$, is obtained by heating the diphthalyl compound in a sealed tube with hydrochloric acid at 200 — 220° for some hours. It is a colourless liquid, having a strong ammoniacal odour, boils at 268° , eagerly absorbs carbonic anhydride from the air, and yields well crystallised salts with acids. The *picrate* crystallises in small, bright yellow needles, and decomposes at 235° . The *platinochloride* crystallises in yellow plates, and decomposes at 258° . The *diacetyl* compound crystallises from chloroform in white needles, melts at 165° , and is easily soluble in hot water, concentrated hydrochloric acid, benzene, and chloroform, and yields a well crystallised platinochloride.

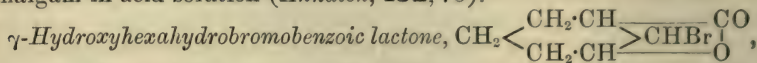
E. C. R.

Hydrobenzoic Acids. By O. ASCHAN (*Annalen*, **271**, 231—284).—In this paper, the author gives a complete account of his work on the reduction products of benzoic acid, and corrects some of the statements made in earlier papers (compare Abstr., 1891, 1053 and 1481); only the new facts are given in this abstract.

In preparing Δ^2 -tetrahydrobenzoic acid by the method already described, hydrobenzoïn (m. p. 134°) is formed in small quantities, as well as benzyl alcohol.

Δ^2 -Tetrahydrobenzoic acid can be distilled in an atmosphere of carbonic anhydride, and then boils at 234 — 235° (mercury entirely in vapour) with very slight decomposition, yielding traces of a neutral liquid, which is probably the lactone of γ -hydroxyhexahydrobenzoic acid. The acid is only sparingly soluble (1.34 grams in 100 c.c.) in water at 20° , and is readily oxidised to benzoic acid on exposure to the air; its electrical conductivity is $K = 0.00305$. The *calcium* salt, $(C_7H_9O_2)_2Ca$, crystallises in needles, and is moderately easily soluble

in cold water, but more sparingly in alcohol. The *silver* salt, $C_7H_5O_2Ag$, is only very sparingly soluble in boiling water, by which it is decomposed; it is very sensitive to light. The *methyl* salt boils at $188-189^\circ$ (mercury entirely in vapour), and has a sp. gr. of 1.0433 at $20^\circ/20^\circ$; it combines readily with bromine in ethereal solution yielding an oil. Δ^2 -Tetrahydrobenzoic acid is identical with the benzoic acid obtained by Herrmann by reducing benzoic acid with sodium amalgam in acid solution (*Annalen*, **132**, 75).



is easily obtained by warming the dibromo-additive product of the Δ^2 -tetrahydro-acid with sodium carbonate; it crystallises from dilute alcohol in long, flat prisms, melts at 67° , and is readily soluble in benzene, ether, alcohol, and glacial acetic acid, but only sparingly in water; it is decomposed by alcoholic potash in the cold with formation of potassium bromide, and a substance which is readily soluble in water, and which decolorises potassium permanganate.

γ -Ethoxy- Δ^1 -tetrahydrobenzoic acid, $C_9H_{14}O_3$, not a dihydrobenzoic acid as at first supposed (Abstr., 1891, 1482), is formed when the dibromo-additive product of the Δ^2 -tetrahydro-acid is treated with alcoholic potash at the ordinary temperature; it crystallises from water in long, transparent prisms, melts at 73° , and is very readily soluble in all ordinary solvents except water; it is immediately oxidised by potassium permanganate in sodium carbonate solution. Its salts are readily soluble and badly characterised. The *silver* salt, $C_9H_{13}O_3Ag$, melts at $130-140^\circ$ when quickly heated, and is stable in the light. The *dibromo*-additive product, $C_9H_{14}Br_2O_3$, is formed, when the acid is treated with bromine in chloroform solution in the dark; it crystallises from a mixture of benzene and light petroleum in large, flat prisms, melts at $125-126^\circ$, and decolorises an alkaline solution of potassium permanganate only after long keeping; its *sodium* salt is only very sparingly soluble in water, from which it crystallises in octagonal prisms. When ethoxy- Δ^1 -tetrahydrobenzoic acid is heated with a saturated glacial acetic acid solution of hydrogen bromide at 100° for 12 hours, it is converted into the dibromohexahydrobenzoic acid (m. p. 166°) previously described.

Hexahydrobenzoic acid (m. p. 28°) can not only be obtained by reducing the mixture of hydrobromo-additive products of the Δ^2 -tetrahydro-acid with sodium amalgam (*loc. cit.*), but also by heating the Δ^2 -tetrahydro-acid with concentrated hydriodic acid at 200° . It boils at $232-233^\circ$ (mercury entirely in vapour), has a disagreeable smell and is very readily soluble in alcohol and ether, but only moderately easily in water; attempts to convert the acid into a stereochemical isomeride were unsuccessful, as was expected. The *silver* salt, $C_7H_{11}O_2Ag$, is a microcrystalline compound, sparingly soluble in boiling water. The *methyl* salt boils at $179-180^\circ$ (mercury entirely in vapour). The *ethyl* salt, $C_8H_{11}COOEt$, is a mobile oil, of sp. gr. 0.9723 at $4^\circ/4^\circ$ and 0.93624 at $20^\circ/4^\circ$; it boils at $194.5-195.5^\circ$ (mercury entirely in vapour).

Δ^1 -Tetrahydrobenzoic acid melts at 29° , and is only sparingly soluble (0.7 gram in 100) in water at 20° ; its sp. gr. is 1.1089 .

at $20^{\circ}/20^{\circ}$, and its electrical conductivity $K = 0.00221$. Its salts are more stable and more sparingly soluble than those of the Δ^2 -tetrahydro-acid. The *silver* salt, $C_7H_5O_2Ag$, crystallises in prisms. The *calcium* salt crystallises in colourless prisms with 1 mol. H_2O , the *ammonium* salt in lustrous plates. The *methyl* salt, $C_6H_5 \cdot COOMe$, is a colourless liquid of sp. gr. 1.05607 at $4^{\circ}/4^{\circ}$, and 1.04183 at $20^{\circ}/4^{\circ}$; it boils at $193.5-194.5^{\circ}$ (mercury entirely in vapour).

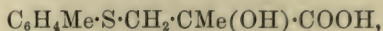
β -Bromohexahydrobenzoic acid, $C_6H_{11}Br \cdot COOH$, is formed, when the Δ^1 -tetrahydro-acid is heated with a saturated glacial acetic acid solution of hydrogen bromide at 100° for 4—5 hours; it crystallises from hot formic acid in large, flat, seemingly rhombic prisms or plates, melts at $108-109^{\circ}$, and decolorises an alkaline solution of potassium permanganate; when boiled with dilute sodium carbonate, it is reconverted into the Δ^1 -tetrahydro-acid.

When the dibromo-additive product of the Δ^1 -tetrahydro-acid is treated with alcoholic potash, it yields an acid which is much more readily soluble in water, and less stable than the Δ^1 -tetrahydro-acid; this product resinifies on keeping, and is probably a dihydro-acid.

A dihydroxyhexahydrobenzoic acid seems to be formed when dibromohexahydrobenzoic acid is dissolved in dilute sodium carbonate ($\frac{1}{2}$ mol.), and the solution then boiled; a small quantity of a neutral oil separates from the solution, but the principal product is an acid which is best isolated in the form of its calcium salt. This compound crystallises from water in large, transparent plates, is almost insoluble in cold water, and has the composition $[C_6H_5(OH)_2 \cdot COO]_2Ca + 2H_2O$; the acid, prepared from the calcium salt, is very hygroscopic, and reduces ammoniacal silver nitrate solution on boiling.

Diacetoxyhexahydrobenzoic acid, $C_6H_5(OAc)_2 \cdot COOH + H_2O$, is obtained when the calcium salt just described is treated with acetic chloride, and the product recrystallised from water; it forms small, monosymmetric crystals, $a : b : c = 3.4176 : 1 : 1.1541$, $\beta = 86^{\circ} 51'$, melts at $72-73^{\circ}$, and loses water when kept over sulphuric acid, being converted into a syrup, which crystallises again on treatment with water; it is readily soluble in alcohol, but more sparingly in cold water. The *silver* salt crystallises in long, slender needles, and is moderately stable in the light. F. S. K.

Organic Sulphur Compounds. By A. DELISLE and A. SCHWALM (*Ber.*, 25, 2980—2984; compare *Abstr.*, 1889, 488).— β -Thioparatothylpropionic acid, $C_6H_4Me \cdot S \cdot CH_2 \cdot CH_2 \cdot COOH$, is obtained quantitatively by boiling ethyl β -iodopropionate with the sodium derivative of parathiocresol in molecular proportion, and hydrolysing the ethyl salt thus formed with alcoholic potash; it crystallises from light petroleum in lustrous plates, and melts at $70-71^{\circ}$. It separates from ether in large, transparent, monosymmetric or asymmetric tablets, and is soluble in most organic solvents. The *silver* salt, $C_{10}H_{11}SO_2Ag$, crystallises from hot water in broad, transparent needles which are fairly stable towards light; the *calcium* salt, $(C_{10}H_{11}SO_2)_2Ca + 3H_2O$, forms white, hair-like needles, and the *barium* salt, $(C_{10}H_{11}SO_2)_2Ba + 2H_2O$, lustrous plates. The *ethyl* salt, obtained in the manner described above, is a thick, yellowish liquid, and boils at 171° under 12 mm. pressure.

α -Hydroxy- β -thiotolylisobutyric acid,

is prepared by the action of hydrogen cyanide on thiotolylacetone, $\text{C}_6\text{H}_4\text{Me}\cdot\text{S}\cdot\text{CH}_2\cdot\text{COMe}$, and hydrolysis of the nitrile thus formed; it crystallises from hot water containing hydrochloric acid in silky, flexible needles, and melts at $101\text{--}102^\circ$. The *calcium* salt crystallises in stellate groups of needles, and the *barium* salt in white plates; the *silver* salt forms a white, curdy precipitate.

The authors have also prepared the ethyl phenylthioacetate (ethyl thiophenylacetoacetate) described by Otto and Rössing, the existence of which has frequently been denied; it is readily obtained by the action of sodium phenylmercaptide on ethyl chloracetoacetate, and is a yellow oil which decomposes at $60\text{--}70^\circ$ with formation of phenyl bisulphide, a reaction which takes place slowly at the ordinary temperature.

Ethyl metethoxyphenylthioacetate, $\text{CHAc}\cdot\text{S}\cdot\text{C}_6\text{H}_4(\text{OEt})\cdot\text{COOEt}$, is obtained by the action of the sodium compound of metethoxyphenyl hydrosulphide (Abstr., 1891, 310) on ethyl chloracetoacetate, and is a pale yellow oil, which, like the preceding compound, readily decomposes with formation of the corresponding bisulphide. *Metethoxyphenyl bisulphide*, $\text{S}_2(\text{C}_6\text{H}_4\cdot\text{OEt})_2$, forms compact crystals melting at $42\text{--}43^\circ$, and may also be obtained by the action of iodine on the hydrosulphide.

β -Thiotolyllevulinic acid, $\text{CHAc}\cdot\text{S}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, is prepared by the action of the sodium derivative of parathiocresol on ethyl β -bromolevulinate, and hydrolysis of the ethyl salt; it melts at $103\text{--}104^\circ$, and yields a *hydrazone* melting at $120\text{--}121^\circ$. The *barium* salt, $(\text{C}_{12}\text{H}_{13}\text{O}_3\text{S})_2\text{Ba}$, crystallises in white, concentric groups of needles.

H. G. C.

Phenylpyruvic Acid and Phenylglycidic Acid. By E. ERLÉNMEYER, Jun. (*Annalen*, 271, 137—180).—In the first part of this paper, the author describes experiments by which he claims to have proved that Glaser's "*phenylhydroxyacrylic acid*" is, in reality, phenylglycidic acid, identical with the compound obtained by Plöchl by treating phenyl- β -bromolactic acid with potash, and considered by him to be α -hydroxycinnamic acid. In the second part of the paper, it is shown that the acid obtained by Plöchl from the condensation product of benzaldehyde and hippuric acid (Abstr., 1884, 604) is identical with phenylpyruvic acid.

When the sodium salt of phenylglycidic acid (Glaser's "*phenylhydroxyacrylic acid*") is covered with ether and treated with dry hydrogen chloride, sodium chloride is deposited, and phenyl- β -chlorolactic acid remains in solution; on fractionally precipitating, with light petroleum, the ethereal solution, previously freed from hydrogen chloride by keeping over potash, the phenyl- β -chlorolactic acid is obtained as an almost colourless oil which soon solidifies. It separates from hot chloroform in small, slender needles, melts at $141\text{--}142^\circ$ with decomposition, and is identical with the acid obtained by Leschhorn (*Inaug. Diss., Würzburg*, 1884), by the action of hydrochloric

acid on phenylglyceric acid; when treated with excess of soda at the ordinary temperature, it is converted into sodium phenylglycidate.

An acid of the composition $C_9H_{11}NO_3$ is formed when sodium phenylglycidate ("sodium phenylhydroxyacrylate") is treated with concentrated ammonia at the ordinary temperature, and the product decomposed with acetic acid; it decomposes at $220-221^\circ$, and is probably a *phenyl- β -amidolactic acid* of the constitution



The acid of the composition $C_{14}H_{19}NO_3$, obtained from sodium phenylglycidate and piperidine in like manner, decomposes at 244° .

Sodium phenylanilidolactate, $C_{15}H_{14}NO_3Na$, can be prepared by treating an aqueous solution of sodium phenylglycidate with aniline, and recrystallising the product from hot alcohol; when treated with dilute acetic acid, it yields phenylanilidolactic acid, melting at $144-145^\circ$.

Phenylglycidic acid can be obtained by adding benzaldehyde and a few drops of alcohol to an ethereal solution of ethyl chloracetate containing sodium in suspension.

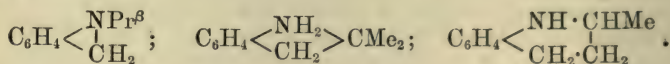
Ethyl phenylcyanopyruvate, $CN \cdot CHPh \cdot CO \cdot COOEt$, is formed when benzyl cyanide is treated with ethyl oxalate and sodium ethoxide in alcoholic solution and the product decomposed with water. It is a crystalline substance, melts at 130° and is soluble in alcohol, soda, ammonia, and sodium carbonate; in its alcoholic solution, ferric chloride produces a dark green coloration; it is readily decomposed by alkalis, yielding benzyl cyanide, but when boiled with moderately concentrated sulphuric acid, it gives phenylpyruvic acid.

F. S. K.

Action of Sulphuric Acid on Quinol. By J. H. STEBBINS, JUN. (*Chem. Centr.*, 1892, ii, 40—41; from *J. Amer. Chem. Soc.*, **13**, 155).—Since the utility of quinol as a photographic developer is considerably impaired by its slight solubility in water, the author has prepared its more soluble sulphonic derivative, $C_6H_3(OH)_2 \cdot SO_3H$, which he has found to act satisfactorily as a developer. It is prepared by heating 10 grams of quinol with 20 grams of sulphuric acid, sp. gr. 1.82, freeing the solid mass from sulphuric acid by means of porous plates and filter paper, and crystallising from a small quantity of alcohol in a vacuum. In forms long, brownish, transparent, rhombic prisms, containing alcohol of crystallisation. Its salts oxidise readily in the air. The barium salt, probably $(C_6H_5O_5S)_2Ba + H_2O$, is most easily prepared; it forms small, white, hexagonal prisms, soluble in cold water and dilute alcohol, and giving with ferric chloride a deep blue coloration, which rapidly changes to dirty-yellow. C. F. B.

Synthesis of 2-Dimethylhydrindole. By C. PAAL and E. LAUDENHEIMER (*Ber.*, **25**, 2974—2978).—Attempts to obtain alkyl derivatives of orthamidobenzyl alcohol by treating it with alkyl iodides having failed, the authors endeavoured to obtain these derivatives by the reduction of the condensation products of the alcohol with aldehydes and ketones (see this vol., p. 23). Isopropyleneorthamidobenzyl

alcohol is readily reduced by sodium in alcoholic solution, with formation of *isopropylorthamidobenzyl alcohol*, $\text{NHPr}^s \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OH}$, which forms a yellowish oil, sparingly soluble in water, but readily in mineral acids and organic solvents. It distils between 210° and 260° , undergoing partial decomposition; if it is boiled in connection with a reflux apparatus for two hours, the decomposition is complete, the products being water and a colourless oil, which has the composition $\text{C}_{10}\text{H}_{13}\text{N}$; it boils at 210° (uncorr.), is almost insoluble in water, but dissolves readily in mineral acids, and has a faint, turpentine-like odour. The elimination of water from isopropylorthamidobenzyl alcohol might take place in three different ways, with formation of the following compounds:—



The first formula cannot, however, represent the constitution of the compound, as it yields a nitroso-derivative, and must, therefore, be a secondary base; the substance represented by the third formula is tetrahydroquinaldine, which has already been prepared (Abstr., 1881, 742; 1884, 183), and has properties quite different from those of the authors' compound. There remains, therefore, only the second formula, according to which the substance is 2-dimethylhydrindole, and with this supposition its properties fully agree.

2-Dimethylhydrindole combines with ethyl iodide to form the *ethiodide*, which separates from ether in well developed prisms. The *nitrosamine*, $\text{C}_{10}\text{H}_{12}\text{N} \cdot \text{NO}$, is a reddish-brown oil, which decomposes on distillation, even in a vacuum; the *hydrochloride*, $\text{C}_{10}\text{H}_{13}\text{N} \cdot \text{HCl}$, crystallises from water in slender, white needles, and melts at 150° with decomposition; the *platinochloride*, $(\text{C}_{10}\text{H}_{13}\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$, crystallises in orange-red plates, melts at 200° with decomposition, and is readily soluble in water.

H. G. C.

Bidiphenylenethylene: A Red Hydrocarbon. By C. GRAEBE (*Ber.*, 25, 3146—3149).—By passing fluorene over heated lead oxide, de la Harpe and van Dorp (this Journal, 1876, i, 242) obtained a red hydrocarbon $\text{C}_{26}\text{H}_{16}$. Mantz (*Inaug. Diss.*, Geneva, 1892) found that the same compound was formed by heating fluorene with bromine at 240 — 300° , or by passing a current of chlorine into fluorene at a temperature of 280 — 290° ; also by heating fluorene with sulphur. He established its molecular weight, and assigned to it the constitution $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} > \text{C} : \text{C} < \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array}$, inasmuch as it combined with two equivalents of halogen, yielded diphenylene ketone on oxidation, fluorene on heating it with zinc dust, and a colourless hydrocarbon $\text{C}_{26}\text{H}_{18}$ on hydrogenation. The author finds that bidiphenylenethylene is best prepared by heating a mixture of lead oxide and fluorene to the boiling point of the latter, and finally for a short time at 350° , extracting the product with carbon bisulphide, and crystallising the residue from alcohol and chloroform or carbon tetrachloride, when the pure hydrocarbon is obtained in yellowish-red needles and prisms, the colour being intermedi-

ate between those of potassium dichromate and chromic anhydride. It melts at $187-188^{\circ}$ (corr.), and cannot be decolorised; indeed further purification tended to increase the brightness of its colour. It forms a colourless dibromide, $C_{26}H_{16}Br_2$, a solution of which in toluene becomes red on warming it with sodium, due to the reproduction of the hydrocarbon. The colour of bidiphenylenethylene is apparently to be ascribed to the presence of the group —C:C— , as both the dibromide and the hydrocarbon $C_{26}H_{18}$ (bidiphenylenethane) are colourless. The atomic grouping of the red hydrocarbon is thus analogous to that of azobenzene, but the doubly-linked carbon atoms exert less influence on the colour than do the doubly-linked nitrogen atoms, inasmuch as diphenylethylene and tetraphenylethylene are both colourless (compare, however, Armstrong, Proc., 1892, 192). Its further study is being continued.

A. R. L.

Derivatives of 1:4-Amidonaphthalene. By R. HENRIQUES (*Ber.*, 25, 3058—3068).—1:4-Nitroethoxynaphthalene (Hermann, Abstr., 1891, 1379; Grandmougin and Michel, Abstr., 1892, 862) is conveniently prepared by dropping α -ethoxynaphthalene into nitric acid of 28° Baumé ($1\frac{1}{2}$ parts) at 60° , the yield being 90 per cent. of the ethoxynaphthalene employed. In addition to the description given of the corresponding amido-derivative (*loc. cit.*), it is to be mentioned that when ferric chloride is added to solutions of its salts, a copious indigo-blue precipitate separates, and on boiling, α -naphthaquinone is formed.

1:4-Acetamidoethoxynaphthalene is economically prepared by adding a mixture of amidoethoxynaphthalene hydrochloride (2 parts) and sodium acetate (3 parts), together with a trace of stannous chloride, to a cold solution of phosphoric chloride (1 part) in glacial acetic acid (4 parts), and boiling for a short time. It crystallises from alcohol or glacial acetic acid in long, colourless needles, melts at 189° , and is as good as insoluble in water, and somewhat sparingly soluble in boiling alcohol. 1:4-Nitromethoxynaphthalene melts at 83° , and the corresponding acetamido-compound melts at 187° . 1:4-Amidoethoxybenzene (phenetidine) is not attacked by nitric acid in the cold, but when boiled with it, the odour of quinone is perceptible; whereas the acetyl derivative (phenacetine), according to Autenrieth and Hinsberg (Abstr., 1892, 160), is converted by dilute nitric acid into the nitro-derivative [$\text{OEt} : \text{NO}_2 : \text{NHAc} = 4 : 2 : 1$], an observation which the author confirms.

When 1:4-acetamidoethoxynaphthalene is treated with cooled nitric acid of 26° Baumé, a compound, $C_{28}H_{34}N_3O_5$, is obtained, which crystallises from alcohol in yellow needles, melts at $218-219^{\circ}$, is insoluble in water and in alkalis, and decomposes with the evolution of acetic acid, if boiled with sulphuric acid. The same compound is obtained together with α -naphthaquinone when 1:4-acetamidoethoxynaphthalene is boiled with dilute nitric acid.

When 1:4-amidoethoxynaphthalene hydrochloride is treated with nitric acid of 20° Baumé (10 parts), α -naphthaquinone separates, whilst on adding ferric chloride and hydrochloric acid to the filtrate, a yellow crystalline precipitate falls, which is sparingly soluble in

alcohol, readily so in water, but reprecipitated on the addition of hydrochloric acid; it is a *double salt* of the diazo-derivative, and similar compounds are obtained on adding chromic acid or mercuric chloride and hydrochloric acid to a solution of diazotised amidoethoxynaphthalene.

When 1 : 4-amidoethoxybenzene (10 grams) is dissolved in a mixture of alcohol (50 grams) and 50 per cent. acetic acid (25 grams), and a 10 per cent. solution of sodium nitrite (26 c.c. = 0.5 mol.) added, the *diazoamido*-derivative, $C_{16}H_{19}N_3O_2$, separates in yellow needles; water is now added, and as soon as the precipitation is complete, the compound is collected and washed successively with water and alcohol. It cannot be recrystallised, as it undergoes decomposition; it melts at 89–91°, and combines with phenols to form hydroxyazo-compounds. The author has not as yet succeeded in converting it into the amidoazo-derivative, but it yields a crystalline compound when treated with alcohol, which will be described in a future paper.

When 1 : 4-amidoethoxynaphthalene is treated with nitrous acid, in the manner just described, it yields *amidoazoethoxynaphthalene*, $C_{24}H_{23}N_3O_2$, which crystallises from benzene in red needles, melts at 175°, and is readily soluble in benzene, sparingly so in alcohol and glacial acetic acid, and insoluble in water. It is a feeble base, yielding yellow salts which dissolve sparingly in alcohol, forming green solutions, dissociate in the air, and are decomposed when boiled with water. On reduction with stannous chloride and hydrochloric acid, a mixture of compounds, which are being further investigated, is obtained; one of the most soluble salts from this mixture yields, on acetylation, a compound $OEt \cdot C_{10}H_5(NHAc)_2$, melting at 254°.

A. R. L.

Action of Phenylhydrazine on Cantharidin. By L. SPIEGEL (*Ber.*, 25, 2956—2960).—The substance obtained in small quantities together with cantharidinphenylhydrazone by the action of phenylhydrazine on cantharidin (Abstr., 1892, 999) may be obtained pure by frequent recrystallisation from acetone and subsequently from absolute alcohol, and drying at a temperature not exceeding 105°. It has then the composition $C_{16}H_{20}N_2O_4$, and melts at 194°; the author proposes for it the name *cantharidinphenylhydrazone hydrate*. When it is heated with an excess of phenylhydrazine, with aniline, with alcoholic potash, or by itself above 105°, it loses the elements of water, forming cantharidinphenylhydrazone. The author believes that the compound is formed by the direct union of phenylhydrazine with the carbonyl group of cantharidin without simultaneous elimination of water, according to which its constitution would be represented by the formula $C_9H_{12}O_3 \cdot C(OH) \cdot NH \cdot NHPh$.

If cantharidin is allowed to remain with an excess of phenylhydrazine at the ordinary temperature, it yields a substance which, although it has not been obtained pure, appears to be the *phenylhydrazone of cantharic acid*, $COOH \cdot C_8H_{12}O \cdot CO \cdot NH \cdot NHPh$. All attempts to purify it by recrystallisation were unsuccessful, owing to the ease with which it passes into cantharidinphenylhydrazone.

H. G. C.

Chlorophyll. Part IV. By E. SCHUNCK (*Proc. Roy. Soc.*, 50, 302—317; compare *Abstr.*, 1887, 972; 1889, 279).—When the residue obtained by evaporating to dryness a solution of phyllocyanin in aqueous potash is heated nearly to fusion, it suddenly turns brown. The aqueous solution of the mass, on treatment with acetic acid, gives a bulky, brown precipitate, which is ultimately obtained in lustrous, plum-coloured needles. It is soluble in concentrated hydrochloric acid, glacial acetic acid, chloroform, ether, or boiling alcohol, and insoluble in carbon bisulphide. The solutions are crimson, and their spectra show no absorption bands at the red end. This substance is possibly identical with Hoppe-Seyler's dichromatic acid or phylloporphyrin.

On treating chlorophyll with concentrated acids, phylloxanthin is formed in addition to phyllocyanin; concentrated hydrochloric acid extracts the latter from the ethereal solution of the two substances, and on exposing the ethereal solution to the air, brown cakes are obtained, which are dissolved in a little chloroform, alcohol added, the deposit washed with alcohol, dried, and dissolved in boiling glacial acetic acid. Phylloxanthin is deposited on cooling and is again dissolved in hot acetic acid, allowed to separate, and after being deposited several times from ether, is obtained as a dark green, amorphous powder still containing a little fatty matter. It sometimes separates from its ethereal solution in small, stellate groups, but is deposited from boiling alcohol in a granular state; it is soluble in ether, carbon bisulphide, benzene, aniline, light petroleum, and chloroform, giving brownish-green, fluorescent solutions. It begins to decompose at 160°, and on burning, leaves a residue of ferric oxide; iron seems to be an essential constituent. Nitric or chromic acid turns its acetic acid solution deep yellow; with concentrated nitric acid, phylloxanthin yields oxalic acid. The chloroform solution is bleached by light on exposure to air; bromine in small quantities turns the chloroform solution bright green, whilst excess of bromine gives a yellow colour. A dark blue solution is obtained with concentrated hydrochloric or sulphuric acid. The reactions with copper acetate, ferrous oxide, silver oxide, metallic tin in acid solution, and alcoholic alkalis are described.

"Alkaline chlorophyll" is best prepared by extracting fresh grass leaves with boiling alcohol (80 per cent.); the solution is filtered hot, and, on cooling, deposits crude chlorophyll. This is boiled for some time with alcoholic soda, filtered, and the filtrate saturated with carbonic anhydride. The precipitate is extracted with cold alcohol, saturated sodium chloride solution added to the solution, the precipitate dissolved in boiling alcohol, and the solution evaporated to dryness. The residue, after washing with a little cold water, is found to be a sodium compound; on treatment with the requisite quantity of acetic acid, extracting with ether, and evaporating the ethereal solution, a green substance free from sodium is obtained. This the author terms *alkachlorophyll*. It is amorphous, soluble in alcohol, ether, chloroform, benzene, carbon bisulphide, or aniline, giving bluish-green solutions exhibiting a red fluorescence; but insoluble in boiling water and light petroleum. Its solutions are

much more stable towards light than are those of chlorophyll. With acetic acid, it seems to yield phyllotaonin.

W. J. P.

Trichosanthin and Thallochlore. By TSCHIRCH (*Chem. Centr.*, 1892, ii, 80; from *Schweiz. Woch. Pharm.*, 30, 221—222).—If the succulent part of the fruit of *Trichosanthes pubera* is extracted with ether, a red pigment is removed, which was only examined spectroscopically. If the residue is now extracted with alcohol, a green pigment, *trichosanthin*, is dissolved out; it can be purified by dissolving it in hydrochloric acid and reprecipitating with water. It is a black powder, and its solution in hydrochloric acid is blue. It is the first green pigment obtained from plants which is not identical with chlorophyll, as thallochlore from the gonidia of *Cetraria islandica* is identical with the latter.

C. F. B.

Affinity Coefficients of some Pyrroline and Indole Acids. By A. ANGELI (*Gazzetta*, 22, ii, 1—31).—The author has measured the electrical conductivity of the acids given in the following table:—

	K.
α -Pyrrolinecarboxylic acid	0·00403
<i>n</i> -Methylpyrrolineglyoxylic acid.....	2·7
α -Acetyl- α -pyrrolinecarboxylic acid.....	0·0305
Metadimethyl- β -pyrrolinecarboxylic acid	0·000075
Paradimethyl- β -pyrrolinecarboxylic acid	0·00011
Metadimethylpyrrolinedicarboxylic acid	0·00213
α -Indolecarboxylic acid	0·0177
β -Indolecarboxylic acid	0·00056
β -Methyl- α -indolecarboxylic acid	0·0047
β -Methyl- β -indolecarboxylic acid	0·00013
Methylindoleacetic acid.....	0·00215
Benzoylpyruvic acid.....	0·65
Phenyloxazolic acid	0·55
Thiophenpyruvic acid	0·46
Pyrrolinepyruvic anhydride	0·089
Bromocitraconic anhydride.....	1·49
Dibromacetylacrylic acid	0·0061
Apiolic acid	0·00803
Apionylketonic acid	3·35
Acetonedicarboxylic acid.....	0·079

In solutions of pyrrolineglyoxylic acid the value of 100 *k* diminishes enormously with increased dilution; this is probably due to the great readiness with which the aqueous solution changes on exposure to the air. The constant *K* is certainly greater than 0·967.

The affinity coefficients of dibromomethylpyrrolineglyoxylic acid and paradimethylpyrrolinedicarboxylic acid are so great that the author was unable to determine them.

The aqueous solution of metadimethyl- α -pyrrolinecarboxylic acid changes so rapidly that concordant results could not be obtained with it.

From the data afforded by the indole- and methylindole-carboxylic acids, the author shows that β -pyrrolinecarboxylic acid should have an

affinity coefficient $K = 0.00012$. It is noteworthy that in all the cases examined, the presence of a methyl group in proximity to the carbonyl group greatly diminishes the affinity coefficient. The very high coefficient found for dibromacetylacrylic acid renders it probable that the substance has the constitution $\text{CBr} \begin{smallmatrix} \text{CBr} \\ \text{COO} \end{smallmatrix} > \text{OMe} \cdot \text{OH}$.

W. J. P.

Action of Piperidine and Pyridine on Haloïd Salts of Cadmium. By R. VARET (*Compt. rend.*, 115, 464—466).—Dry and finely powdered cadmium chloride slowly combines with piperidine at 25° and yields a bulky, white, amorphous compound, $\text{CdCl}_2 \cdot 2\text{C}_5\text{H}_{11}\text{N}$, very slightly soluble in piperidine, decomposed by water, and unstable when exposed to air. Cadmium bromide under similar conditions yields small, hard, brilliant, white crystals of the compound $\text{CdBr}_2 \cdot 2\text{C}_5\text{H}_{11}\text{N}$, which is decomposed by water. If warm piperidine is saturated with cadmium bromide, the compound $\text{CdBr}_2 \cdot 3\text{C}_5\text{H}_{11}\text{N}$ separates in small crystals on cooling; it alters when exposed to air, and is only slightly soluble in piperidine. Cadmium iodide yields two analogous crystalline compounds.

Pyridine with cadmium chloride yields only the compound $\text{CdCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$; cadmium bromide yields the compound $\text{CdBr}_2 \cdot 6\text{C}_5\text{H}_5\text{N}$; cadmium iodide, the compound $\text{CdI}_2 \cdot 6\text{C}_5\text{H}_5\text{N}$.

C. H. B.

Action of Bromine on Aldehydecollidine. By P. KNUDSEN (*Ber.*, 25, 2985—2989).—*Bromethyl- α -picoline*, $\text{C}_5\text{NH}_3\text{Me} \cdot \text{CHMeBr}$, is obtained by heating aldehydecollidine (10 grams) dissolved in the calculated quantity of concentrated hydrochloric acid with bromine (26.5 grams) for 10—12 hours at 100° . The product is dissolved in ether, treated with sulphurous acid, and excess of soda added. The ethereal solution is then separated, shaken with dilute acetic acid, then with dilute alkali, and dried over calcium chloride. On distilling the ether in a vacuum, a thick, bright-yellow oil is obtained which has an aromatic, disagreeable, penetrating odour, and is too unstable to be analysed. The *picrate* crystallises from benzene in compact prisms or needles, and melts at 154° .

α -Picolyl- β_1 -methylalkine, $\text{C}_5\text{NH}_3\text{Me} \cdot \text{CHMe} \cdot \text{OH}$, is obtained as *picrate* on boiling the above bromocollidine *picrate* with a large quantity of water. It crystallises in broad leaflets or tablets, and melts at 164° . The *free base* is obtained by cautiously treating the *picrate* with a solution of sodium hydroxide and then extracting with ether. It boils at 240° with slight decomposition, is a colourless, viscid oil, soluble in water, and solidifies to a crystalline mass which melts at blood-heat. When oxidised in the cold with dilute permanganate, it yields methylnicotinic acid (m. p. 209—210°).

50 grams of aldehydecollidine yield 110 grams of crude bromocollidine *picrate* and 31 grams of crude, or 14 grams of the pure alkine boiling at 240° .

α -Picolyl methyl ketone, $\text{C}_5\text{NH}_3\text{Me} \cdot \text{COMe}$, is obtained by oxidising the above alkine dissolved in acetic acid with the calculated quantity of chromic acid dissolved in acetic acid (50 per cent.) at 60 — 70° . It boils at 230 — 240° , is a colourless limpid liquid, quickly turns brown,

and is easily soluble in water. The *oxime*, which is sparingly soluble in water, crystallises from dilute alcohol in beautiful needles, and melts at 182° .
E. C. R.

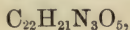
Oxidation of Quinoline by Potassium Permanganate. By A. GOLENKHIN and A. KLEPIKOFF (*J. Russ. Chem. Soc.*, **22**, 535—548).—Quinoline prepared synthetically by Skraup's reaction, when oxidised by permanganate solution, whether hot (60°) or cold, gives nothing but quinolinic and oxalic acids, no other crystalline acid being formed. The yield of quinolinic acid varies, according to the proportions of quinoline and permanganate taken, from 11 to 23 per cent. of the quinoline employed, the greatest yield being obtained with 6.66 mols. of permanganate to 1 mol. of quinoline, and a 3.7 per cent. solution of the oxidant. Cooling does not increase the yield. When coal-tar quinoline is oxidised in the same way, other crystalline acids, besides oxalic and quinolinic, are formed; one of these melts at 168° .
J. W.

New Synthesis of Pyrazole Derivatives. By A. BISCHLER (*Ber.*, **25**, 3143—3145).—The formation of hydrazones from ethyl acetoacetate or its alkyl derivatives, and diazobenzene salts, has been observed by Japp and Klingemann, and by V. Meyer. If a concentrated aqueous solution of diazobenzene chloride (1 mol.) is slowly poured, with cooling, into mixed alcoholic solutions containing equivalent proportions of ethyl acetophenoneacetoacetate (Paal, *Abstr.*, 1884, 598) and sodium, and after remaining for half an hour, an excess of water is added to the mixture, an oil separates which at the end of 24 hours is washed with water, redissolved in alcohol, and digested with sodium hydroxide, whereby Beyer and Claisen's diphenylpyrazolecarboxylic acid (*Abstr.*, 1887, 944) is isolated. When the acid is heated above its melting point, 1:5-diphenylpyrazole (*loc. cit.*) is formed; the latter is readily soluble in alcohol, ether, and benzene, but insoluble in water, and yields a crystalline platinum-chloride.
A. R. L.

Oxazine Dyes. By R. NIETZKI and A. BOSSI (*Ber.*, **25**, 2994—3005).—The authors propose to modify the nomenclature of these compounds as given by Möhlau (*Abstr.*, 1892, 887). They propose to substitute the name *oxazone* for quinoxazone and *oxazime* for quinoxazine. For the corresponding compounds of the methylene-blue series, they propose the names *thiazone* and *thiazime*; and they designate derivatives in which the imido-group is replaced by the ammonium group by changing the ending "azime" into "azimium."

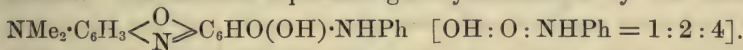
Nietzki and Otto (*Ber.*, **21**, 1745) have stated that 2 mols. of aniline combine with gallocyanin with elimination of 1 mol. H_2O . On repeating the experiment, the authors find that only 1 mol. of aniline combines with elimination of 1 mol. of carbonic anhydride and 1 mol. of hydrogen and a compound of the formula $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_3$ is obtained. By conducting the experiment in a suitable apparatus, an absorption of atmospheric oxygen is observed; but the yield (50—60 per cent.) is the same whether the experiment is performed in air or in an atmosphere of carbonic anhydride.

The methyl ether of gallocyanin, "prune," combines in molecular proportion with aniline, giving a compound of the formula



and in this reaction no absorption of oxygen is observed.

If gallocyanin and aniline are rubbed together in the cold, a crystalline compound is formed without evolution of carbonic anhydride; this compound is not a simple aniline salt of gallocyanin, for when treated with dilute hydrochloric acid gallocyanin is not regenerated. The compound cannot be purified by crystallisation, and when gently heated is converted into gallocyanin-anilide. The authors represent gallocyaninanilide by the formula



Meldola's naphthol-blue combines with 1 mol. of aniline with evolution of 1 mol. of hydrogen. The commercial zinc double salt of Meldola's blue is converted into nitrate by means of dilute nitric acid, and the nitrate warmed with excess of aniline on the water-bath. This nitrate is converted first into the base, and then into hydrochloride.

The *hydrochloride* is somewhat sparingly soluble in water and cold alcohol, crystallises from hot alcohol in long needles having a green lustre, and must be crystallised in the presence of hydrochloric acid, as it tends to decompose in solution. The *free base* is obtained in slender, shining, brown needles by adding ammonia to a hot alcoholic solution of the hydrochloride; it melts at 275° and is insoluble in water and hot alcohol. The salts impart to animal fibres and cotton mordanted with tannin a greenish-blue shade, which is changed to red by dilute alkalis. The base most probably has the constitution

$\text{NMe}_2 \cdot \text{C}_6\text{H}_3 < \overset{\text{O}}{\text{N}} > \text{C}_{10}\text{H}_5 \cdot \text{NPh}$, and is therefore a phenylated Nile-blue, and should be obtained by the action of nitroso-dimethylmetamidophenol on phenyl- α -naphthylamine. The authors have prepared the compound by the latter method, and find that the two preparations are identical, giving the same melting point and the same absorption spectra.

From the above results, the authors conclude that Witt's cyanamine obtained by the action of dimethylparaphenylenediamine on Meldola's blue is a dimethylamido-derivative of the above compound, and has the formula $\text{NMe}_2\text{Cl} : \text{C}_6\text{H}_3 < \overset{\text{O}}{\text{N}} > \text{C}_{10}\text{H}_5 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$.

Muscarine behaves in a very similar manner to Meldola's blue. The *hydrochloride* is sparingly soluble in cold water, more easily in hot water, crystallises in slender, violet needles, and has the composition $\text{NMe}_2\text{Cl} : \text{C}_6\text{H}_3 < \overset{\text{N}}{\text{O}} > \text{C}_{10}\text{H}_5 \cdot \text{OH}(\beta)$. The free base is obtained by adding ammonia to a solution of the salt, and forms a precipitate having a violet lustre; it is soluble in potassium or sodium hydroxide.

Aniline combines with the salts of muscarine with even greater readiness than with those of Meldola's blue. The *hydrochloride* of

the compound thus produced has the composition $C_{24}H_{20}N_3O_2Cl$, crystallises in green needles, and dissolves in alcohol with a greenish-blue coloration. The *free* base is obtained in needles having a brown lustre and gives red solutions. E. C. R.

Indazole Derivatives. By O. N. WITT, E. NOELTING, and E. GRANDMOUGIN (*Ber.*, **25**, 3149—3156; compare Abstr., 1891, 312).—Acetylnitroindazole (*loc. cit.*) crystallises from alcohol in long, flat needles, melts at 140° , and yields amidindazole (m. p. 210°) on treatment with alcoholic ammonium sulphide.

Acetamidindazole, $NHAc \cdot C_6H_3 < \begin{smallmatrix} CH \\ | \\ N- \end{smallmatrix} > NH$, formed by boiling the last-mentioned amidindazole with glacial acetic acid for 12 hours, crystallises from alcohol in long, white needles, melts at 248° , sublimes undecomposed, but undergoes oxidation in solution. It dissolves in concentrated hydrochloric acid, and the solution diluted with water is only diazotised on boiling it with nitrite; the compound may be readily diazotised after heating it with sodium hydroxide solution.

Acetamidoacetylindazole, $NHAc \cdot C_6H_3 < \begin{smallmatrix} CH \\ | \\ N- \end{smallmatrix} > NAc$, is obtained, together with the last described derivative, when the amidindazole is boiled with acetic anhydride for some time, and being less soluble in water than acetamidindazole, separates from the solvent in slender, felted needles, melts at 184 — 185° , and distils undecomposed. It is soluble in an excess of concentrated hydrochloric acid, is not precipitated on adding water, and cannot be diazotised until it is hydrolysed.

In the preparation of hydroxyindazole (*loc. cit.*), it is advisable to employ a fairly concentrated solution, and after boiling the diazo-solution, to neutralise it before extracting with ether. It crystallises from boiling water in lustrous leaflets, melts at 215 — 216° , and its alkaline solution, on the addition of diazosulphanilic acid, gives an orange-red colouring matter. No trace of an indazole derivative is formed by heating the diazo-derivatives of nitrometaxyline [$Me_2 : NO_2 : NH_2 = 1 : 3 : 4 : 6$] or nitrothotoluidine [$Me : NO_2 : NH_2 = 1 : 4 : 6$].

The *diazoamido*-derivative of nitrotoluidine [$Me : NH_2 : NO_2 = 1 : 2 : 4$] is prepared by dissolving the nitrotoluidine (31 grams) in glacial acetic acid (400 c.c.) and adding by degrees an aqueous solution of sodium nitrite (7 grams) to the cooled solution. It is insoluble in water, and only sparingly soluble in most solvents. It is best purified by very cautiously crystallising it from hot glacial acetic acid, from which it separates in yellow needles; it melts at 200 — 201° with the evolution of gas. When boiled for a long time with glacial acetic acid (5 parts), nitroindazole (m. p. 177 — 178°) is formed; (compare Heusler, Abstr., 1892, 456). A. R. L.

2'-Paratolyindazole. By C. PAAL and E. FRITZWEILER (*Ber.*, **25**, 3167—3172; compare Abstr., 1891, 723; 1892, 67).—2'-Paratoly-

indazole, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH} \\ \text{N} \end{smallmatrix}\rangle\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$, is obtained by boiling equal weights of orthonitrobenzylparatoluidine (Lellmann and Stickel, Abstr., 1886, 793), dissolved in alcohol, with tin and hydrochloric acid until dissolution is complete, gently warming the *stannochloride* which separates on cooling with an excess of ammonium polysulphide, and diluting with water, when a mixture of the base and tin sulphide is precipitated. On extracting this with boiling absolute alcohol, the indazole separates from the filtrate in long, white, lance-shaped crystals; it melts at 105° , distils undecomposed, and is insoluble in water. It has only feeble basic properties; the *hydrochloride* crystallises from concentrated hydrochloric acid in white needles, and is dissociated by water.

Paratolueneorthazobenzoic acid, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, is formed when the indazole, dissolved in glacial acetic acid, is treated with rather more than 2 mol. proportions of chromic anhydride in the same solvent. On adding water, it separates as an oil which subsequently solidifies; this is dissolved in dilute ammonia and reprecipitated by hydrochloric acid. The pure compound crystallises from dilute alcohol in red needles, and melts at 115° . The *alkali* salts are soluble in water, and their solutions give no precipitates with calcium, barium, or magnesium salts, but a red, flocculent precipitate with aluminium chloride, and an orange precipitate with silver nitrate.

Paratoluenehydrazobenzoic acid, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, is produced by gently warming a dilute ammoniacal or alcoholic solution of the azo-acid with zinc dust. It crystallises from dilute alcohol in yellowish leaflets, melts at 144° , and its solutions oxidise in the air. The *alkali* salts are soluble in water, and their solutions give with barium chloride a white precipitate soluble on boiling; silver nitrate gives a white precipitate which immediately becomes black. An *acid* isomeric with that just described is obtained when a dilute alcoholic solution of paratolueneorthoazobenzoic acid is boiled with tin and hydrochloric acid. It crystallises from ethyl acetate in bunches of white needles, and melts at 198° . The *alkali* salts are soluble in water, and the *silver* salt is a white precipitate which only gives a metallic mirror on heating. The constitution of the acid is being determined.

A. R. L.

Phenometadiazine Derivatives. By A. BISCHLER and D. BARAD (*Ber.*, 25, 3080—3097; compare Bischler, Abstr., 1891, 745).—Acetylorthamidobenzophenone melts at $88.5\text{--}89^\circ$, not at 72° as stated by Auwers and Meyenburg (Abstr., 1891, 1375); it is readily soluble in ether, hot alcohol, and hot benzene, but insoluble in cold water.

Pheno-2'-methyl-4'-phenylmetadiazine, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CPh}\cdot\text{N} \\ \text{N}=\text{CMe} \end{smallmatrix}\rangle$, is obtained when acetylorthamidobenzophenone is heated at 170° for three hours with concentrated alcoholic ammonia; it is a yellowish, crystalline compound, melts at $47\text{--}48^\circ$, boils at $349\text{--}353^\circ$, and is readily soluble

in alcohol, ether, and benzene, but almost insoluble in water. A vapour density determination, carried out under reduced pressure, gave results which showed that its molecular formula is $C_{15}H_{12}N_2$. It is not decomposed by concentrated hydrochloric acid even at $200-210^\circ$. The *hydrochloride*, $C_{15}H_{12}N_2 \cdot HCl$, prepared by passing hydrogen chloride into an ethereal solution of the base, separates from alcoholic ether in colourless crystals, and is very readily soluble in water and alcohol, but insoluble in ether. The *platinochloride*, $(C_{15}H_{12}N_2)_2 \cdot H_2PtCl_6$, crystallises from hot alcohol in flat, orange needles, decomposes at 160° , and is readily soluble in hot alcohol, but almost insoluble in cold water. The *picrate*, $C_{15}H_{12}N_2 \cdot C_6H_3N_3O_7$, crystallises from hot dilute alcohol in dark yellow needles, decomposes at 170° , and is only sparingly soluble in boiling water. The *mercu-rochloride*, $C_{15}H_{12}N_2 \cdot HgCl_2 + H_2O$, separates from hot water in lustrous, greyish needles, and loses its water at $100-115^\circ$. The *methiodide*, $C_{15}H_{12}N_2 \cdot MeI$, is formed when the base is heated with methyl iodide at 120° ; it separates from hot alcohol in the form of a heavy powder, melts at 190° , and is rather sparingly soluble in cold water, alcohol, and ether. The *ethiodide*, $C_{15}H_{12}N_2 \cdot EtI$, forms lemon-yellow needles, melts at 204° , and is rather more readily soluble in warm alcohol and water than the methiodide.

Propionylorthamidobenzophenone, $COEt \cdot NH \cdot C_6H_4 \cdot COPh$, prepared by warming the amidoketone with propionic anhydride, crystallises from dilute alcohol in lustrous, colourless needles, melts at 78.5° , and is readily soluble in hot alcohol, benzene, and ether.

Pheno-2'-ethyl-4'-phenylmetadiazine, $C_{16}H_{14}N_2$, prepared by heating the preceding compound at 170° with alcoholic ammonia, crystallises from hot dilute alcohol in flat, colourless needles, melts at 83° , and is soluble in 12.01 parts of 94 per cent. alcohol at 19° , and in 11.18 parts of benzene at the same temperature; molecular weight determinations by the freezing point and by the vapour density methods gave results agreeing with those required by a compound of the above molecular formula. The *platinochloride*, $(C_{16}H_{14}N_2)_2 \cdot H_2PtCl_6$, crystallises from hot dilute alcohol in small, yellow plates, decomposes at about $200-205^\circ$, and is insoluble in ether, but readily soluble in boiling alcohol and water. The *picrate*, $C_{16}H_{14}N_2 \cdot C_6H_3N_3O_7$, crystallises from hot alcohol in long, yellow needles, and decomposes at 150° ; it dissolves freely in hot water and alcohol.

Butyrylorthamidoacetophenone, $COPr \cdot NH \cdot C_6H_4 \cdot COPh$, separates from alcohol in well-defined, colourless, rhombic crystals, melts at 56° , and dissolves freely in hot ether, alcohol, and benzene, but only sparingly in the cold solvents.

Pheno-2'-propyl-4'-phenylmetadiazine, $C_{17}H_{16}N_2$, crystallises from hot dilute alcohol in yellowish needles, melts at $99-100^\circ$, and is soluble in 11.37 parts of 94 per cent. alcohol and in 11.58 parts of benzene at 19° . The *platinochloride*, $(C_{17}H_{16}N_2)_2 \cdot H_2PtCl_6$, is a reddish-yellow, crystalline compound, melts at 203° , and is only sparingly soluble in water and alcohol. The *picrate*, $C_{17}H_{16}N_2 \cdot C_6H_3N_3O_7$, crystallises in microscopic, light yellow needles, sinters at 140° , melts at 150° with decomposition, and is readily soluble in hot water and alcohol. The *mercu-rochloride*, $C_{17}H_{16}N_2 \cdot HgCl_2 + H_2O$, separates from boiling

water, in which it is only sparingly soluble, in lustrous, colourless needles, and loses its water at 100° .

Pheno-2'-isopropyl-4'-phenylmetadiazine, $C_{17}H_{16}N_2$, is formed when the oily product of the action of orthamidobenzophenone on isobutyric anhydride is heated with alcoholic ammonia at 170° ; it crystallises from alcohol in well-defined needles, and melts at 99° . The *platinochloride*, $C_{17}H_{16}N_2 \cdot H_2PtCl_6$, is a vermilion-coloured powder, melting at 160° with previous decomposition. The *picrate*, $C_{17}H_{16}N_2 \cdot C_6H_3N_3O_7$, crystallises from alcohol in yellow needles, melts at 140° with decomposition, and is only sparingly soluble in cold water or alcohol.

Benzoylorthamidoacetophenone, $NHBz \cdot C_6H_4 \cdot COPh$, crystallises from dilute alcohol in colourless needles, and melts at 80.5° ; it is readily soluble in warm benzene and alcohol, but only sparingly in ether or cold alcohol.

Pheno-2'-4'-diphenylmetadiazine, $C_{20}H_{14}N_2$, prepared by heating the preceding compound with alcoholic ammonia, crystallises from alcohol in long, colourless needles, sinters at 119° , and melts at 120° ; it is soluble in 21.85 parts of 94 per cent. alcohol and in 15.64 parts of benzene at 17° , and dissolves freely in hot concentrated hydrochloric acid. The *platinochloride*, $(C_{20}H_{14}N_2)_2 \cdot H_2PtCl_6$, is a reddish, crystalline powder only sparingly soluble in hot alcohol; it melts at 180° . The *picrate*, $C_{20}H_{14}N_2 \cdot C_6H_3N_3O_7$, is a yellow powder.

Pheno-4'-phenylmetadiazine-2'-carboxylic acid is obtained in small quantities when phenoethylphenylmetadiazine is oxidised with chromic acid in sulphuric acid solution; it is a yellow, crystalline compound, and readily undergoes decomposition with liberation of carbonic anhydride and formation of pheno-4'-phenylmetadiazine. The *silver salt*, $C_{14}H_9N_2 \cdot COOAg$, is a voluminous, amorphous compound.

Pheno-4'-phenylmetadiazine picrate, $C_{14}H_{10}N_2 \cdot C_6H_3N_3O_7$, crystallises from hot dilute alcohol in small, yellow plates, melts at 178° , and is only sparingly soluble in cold water and alcohol, but readily in the hot solvents.

Tetrahydropheno-2'-methyl-4'-phenylmetadiazine is formed when phenomethylphenylmetadiazine is reduced with sodium and boiling amyl alcohol; it is a brown oil, dissolves freely in the ordinary organic solvents, and gives badly characterised salts with the usual reagents. The *dibenzoyl* derivative, $C_{29}H_{24}N_2O_2$, prepared by heating the base with benzoic anhydride on the water-bath, separates from alcohol in almost colourless needles, melts at $188-189^{\circ}$, and is only sparingly soluble in cold alcohol, but readily in hot alcohol, ether, and benzene. When heated with concentrated hydrochloric acid at $140-150^{\circ}$, it is decomposed into benzoic acid and tetrahydropheno-methylphenylmetadiazine; the *picrate* of the regenerated hydro-base was obtained in yellow plates melting at 197° . F. S. K.

Quinazolines. By C. WOLFF (*Ber.*, 25, 3030—3040).—An extension of Gabriel and Jansen's work (*Abstr.*, 1890, 1442; 1892, 217). Orthonitrobenzylphthalimide is prepared by heating a finely pulverised, intimate mixture of orthonitrobenzyl chloride (40 grams), potassium phthalimide (50 grams), and sodium chloride (135 grams), contained in a dry flask at 140° for about half an hour, and finally

raising the temperature to 170° . The product is extracted with boiling water, and the residue washed with 96 per cent. alcohol, when an amount of the phthalimide remains corresponding with 85 per cent. of the orthonitrobenzyl chloride employed. Orthonitrobenzylamine hydrochloride is obtained by heating equal weights of orthonitrobenzylphthalimide, hydrochloric acid (sp. gr. 1.19), and glacial acetic acid in a sealed tube at 170 – 190° for three hours; the crude product is washed with water to remove phthalic acid, and finally crystallised from 96 per cent. alcohol.

Gabriel and Jansen (*loc. cit.*) have noted the formation of phenylquinazoline and other compounds by the distillation of orthamidobenzylbenzamide. The author finds that when the last-named base is carefully heated at 250° until water ceases to be evolved, *dihydro-2'-phenylquinazoline*, $C_6H_4 < \begin{smallmatrix} CH_2 \cdot NH \\ | \\ N = CPh \end{smallmatrix}$, is obtained; it crystallises from

benzene in flat tables, and is soluble in the ordinary solvents. The *picrate* forms bright yellow needles, and melts at 161 – 162° ; whilst the *platinochloride* is sparingly soluble in water, and melts at 210° .

Tetrahydro-2'-phenylquinazoline, $C_6H_4 < \begin{smallmatrix} CH_2 \cdot NH \\ | \\ NH \cdot CHPh \end{smallmatrix}$, is formed when the dihydro-compound (2.5 grams) is dissolved in alcohol (90 c.c.), and sodium (9 grams) gradually added; after crystallisation from light petroleum, it melts at 99 – 101° , is soluble in all ordinary solvents except water, and is readily decomposed by acids into benzaldehyde and orthobenzylenediamine, so that salts could not be prepared.

Orthonitrobenzylorthotoluylamide, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot CO \cdot C_6H_4Me$, is prepared by shaking together in a closed flask an aqueous solution of orthonitrobenzylamine hydrochloride (1 mol.), a solution of sodium hydroxide (2 mols.), and orthotoluic chloride (1 mol.), collecting the product, and crystallising it from alcohol; it forms brilliant, colourless needles, and melts at 134 – 135° . *Orthamidobenzylorthotoluylamide* is obtained when a solution of the nitro-compound (40 grams) in 96 per cent. alcohol (10 parts) is mixed with an equal volume of hydrochloric acid (sp. gr. 1.13) and some zinc scraps, and the mixture kept cool for several hours. On shaking the clear solution with potash, the base separates as an oil, which is taken up with ether, whence it is isolated in a solid form; it crystallises from benzene in almost colourless needles, and melts at 114 – 116° . The *hydrochloride* melts at 211 – 214° , and the *platinochloride* at 208° . Under no conditions, either by heating the base or by the action of dehydrating agents, could it be converted into a quinazoline derivative.

Orthonitrobenzylparatoluylamide, prepared in the same way as the orthotoluyl derivative, melts at 140 – 142° , and remains unaltered when treated with zinc and hydrochloric acid, tin and hydrochloric acid, ammonium sulphide at 150° , or boiling hydroiodic acid.

Orthonitrobenzylpropionamide, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot COEt$, is prepared by boiling orthonitrobenzylamine hydrochloride (12 grams) with anhydrous sodium propionate (8 grams) and propionic acid (36 c.c.) for half an hour, neutralising the diluted solution with sodium

carbonate, dissolving the precipitated oil in ethyl acetate, and fractionally precipitating the compound with light petroleum; it crystallises in plates, melts at 61—62°, and is almost insoluble in water. *Orthamidobenzylpropionamide* is formed when tin and hydrochloric acid are added to an alcoholic solution of the nitro-compound, and the mixture kept cool for some hours; it melts at 68—70°, and the *platinochloride* melts at 184°. *Dihydro-2'-ethylquinazoline*, $C_6H_4 < \begin{smallmatrix} CH_2 \cdot NH \\ | \\ N = C Et \end{smallmatrix}$, is obtained when the last-mentioned

base is heated until water ceases to be evolved, and then distilled. It passes over at 290—300°, and, when crystallised from benzene, melts at 99—102°; the *tetrahydro-derivative*, $C_6H_4 < \begin{smallmatrix} CH_2 \cdot NH \\ | \\ NH \cdot CH Et \end{smallmatrix}$, formed by reducing it in the manner described above under *tetrahydrophenylquinazoline*, melts at 86—88°.

Orthonitrobenzylethylamine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH Et$, is produced when a solution of orthonitrobenzyl chloride (15 grams) in absolute alcohol (150 c.c.) is heated on the water-bath for three hours in a closed vessel with 33 per cent. ethylamine solution (45 c.c.); the *hydrochloride* melts at 184—186°. *Orthonitrobenzylethylformamide*,



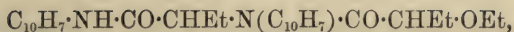
is obtained by boiling a mixture of the last-named base and dry sodium formate with absolute formic acid for four hours; after crystallisation from water, it melts at 65—67°. *Dihydro-3'-ethylquinazoline*, $C_6H_4 < \begin{smallmatrix} CH_2 \cdot N Et \\ | \\ N = CH \end{smallmatrix}$, is formed when the formyl derivative is reduced with zinc and hydrochloric acid; the *picrate* melts at 170—172°, and the *platinochloride* at 199—202°. A. R. L.

Action of Alcoholic Potash on the Anilides, Toluidides, and Naphthalides of α -Bromopropionic, α -Bromobutyric, and α -Bromoisobutyric Acids. By A. TIGERSTEDT (*Ber.*, 25, 2919—2931).—The brominated acid anilides, &c., used were prepared by the action of a chloroform or toluene solution of the base on a similar solution of the brominated acid bromide.

Derivatives of α -Bromopropionyl, $NXH \cdot CO \cdot CHBr \cdot CH_3$.—The *anilide* forms colourless prisms, melting at 99°, sparingly soluble in light petroleum, easily so in chloroform, ether, alcohol, and benzene (see also *Abstr.*, 1892, 1337). The *orthotoluidide*, $CHMeBr \cdot CO \cdot NH \cdot C_6H_4Me$, forms matted needles, insoluble in light petroleum, soluble in alcohol, benzene, ether, and chloroform, and melting at 131°. By the action of alcoholic potash, it yields two isomeric *diorthotolyl- $\alpha\gamma$ -diketo- $\beta\delta$ -dimethylpiperazines*, $C_6H_4Me \cdot N < \begin{smallmatrix} CHMe \cdot CO \\ CO \cdot CHMe \end{smallmatrix} > N \cdot C_6H_4Me$. Of these, the *para-modification* melts at 183—184°, and yields glistening scales, sparingly soluble in ether; the *anti-modification* forms small, agglomerated crystals melting at 155—162°, and more readily soluble in most solvents than the *para-modification*. The *paratoluidide* forms glistening scales, easily soluble in alcohol and chloroform, less so in benzene

and ether, insoluble in light petroleum. With alcoholic potash, it yields the two corresponding piperazines obtained by Goldblatt from paratoluidopropionic acid (Abstr., 1892, 1337). The α -naphthalide is soluble in alcohol, sparingly so in chloroform, benzene, and ether, crystallises in needles, and melts at 158° . With potash, it yields α -dinaphthyl- $\alpha\gamma$ -diketo- $\beta\delta$ -dimethylpiperazine, which was obtained in only one modification crystallising in plates melting at 220 – 224° . From the mother liquors from this piperazine, a substance was isolated which crystallised in rhombic plates melting at 140° with the evolution of a gas. On further heating, the liquid solidified again between 150° and 160° , and eventually fused with decomposition at 207 – 209° . The substance of melting point 207 – 209° had the composition $C_{11}H_{11}NO_2$. The β -naphthalide forms micaceous needles melting at 174° , sparingly soluble in ether and benzene, easily so in alcohol and chloroform; with alcoholic potash, it yields a single β -dinaphthyl- $\alpha\gamma$ -diketo- $\beta\delta$ -dimethylpiperazine, crystallising from chloroform in needles, and melting at 268 – 270° . From the mother liquors of the piperazine, a compound, $C_{11}H_{11}NO_2$, was isolated, analogous to that obtained from the α -naphthylide; this substance is rather more soluble than the α -compound, crystallises in colourless needles, and melts at 191 – 193° . These compounds are probably formed according to the equation $C_{13}N_{12}NOBr + KOH + H_2O = KBr + C_{11}H_{11}NO_2 + C_2H_4O$. The author is further investigating them.

Derivatives of α -Bromobutyryl, $NXH \cdot CO \cdot CHBr \cdot CH_2 \cdot CH_3$. — The *anilide* crystallises in needles melting at 98° . It yields with alcoholic potash the diphenyl- $\alpha\gamma$ -diethyl- $\beta\delta$ -diketopiperazine (m. p. 260°), obtained by Nastvogel from anilidobutyric acid (Abstr., 1890, 1160). The *orthotoluidide* crystallises from hot light petroleum in agglomerated needles melting at 109° , and yields with alcoholic potash two *diorthotolyl- $\alpha\gamma$ -diketo- $\beta\delta$ -diethylpiperazines*. The *para*-modification forms small prisms melting at 218° , soluble in chloroform, benzene, and alcohol, insoluble in ether and light petroleum. The *anti*-modification forms slightly more soluble prisms melting at 178 – 180° . The separation of the two isomerides was effected by treatment with water and alcohol. The *paratoluidide* crystallises from alcohol in prisms melting at 92.5° , and with potash yields the two *diparatolyl- $\alpha\gamma$ -diketo- $\beta\delta$ -diethylpiperazines* obtained from α -orthotoluidobutyric acid (Abstr., 1892, 1338). The α -naphthalide crystallises from alcohol in needles, and melts at 151° ; with potash, it yields a crystalline *di- α -naphthyl- $\alpha\gamma$ -diketo- $\beta\delta$ -dimethylpiperazine* melting at 287 – 289° , together with α -ethoxybutyro- α -naphthalide, $C_{10}H_7 \cdot NH \cdot CO \cdot CH(OEt) \cdot C_2H_5$, which is insoluble in water and light petroleum, and crystallises in needles melting at 79 – 80° . The β -naphthalide forms matted needles melting at 134° , and on treatment with potash yields the *para*-modification of *di- β -naphthyl- $\alpha\gamma$ -diketo- $\beta\delta$ -diethylpiperazine*, which crystallises in needles, and melts at 306° . By long continued digestion with concentrated alcoholic potash, the *para*- is converted into the *anti*-modification melting at 246 – 247° , and crystallising in microscopic prisms. The mother liquors of the *para*-compound contain α -ethoxybutyro- β -naphthalido- α -butyro- β -naphthalide,

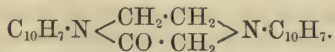


which is insoluble in water and light petroleum, easily soluble in alcohol, ether, &c., crystallises in needles, and melts at 106—110°. The isolation of this compound shows that the formation of the piperazine takes place in two stages.

Derivatives of α -Bromisobutyryl, $\text{NHX}\cdot\text{CO}\cdot\text{CMe}_2\text{Br}$.—No piperazine could be obtained from the anilide, α -hydroxy- and α -ethoxy-isobutyric acids only being formed. The *orthotoluidide* crystallises from chloroform in prisms, and melts at 63°. The action of alcoholic potash yielded α -ethoxyisobutyrothotoluidide and isobutyrothotoluidide. The *paratoluidide* crystallises from alcohol in prisms, and melts at 90°. With alcoholic potash, it yielded α -hydroxyisobutyroparatoluidide, crystallising in cubes, and melting at 132—133°. The α -naphthalide crystallises from chloroform in needles melting at 116°. With alcoholic potash, it yielded α -ethoxyisobutyro- β -naphthalide, which forms soluble prisms melting at 74—76°. The β -naphthalide crystallises from benzene in needles melting at 135°. With alcoholic potash, it yielded α -hydroxy- and α -ethoxy-isobutyro- β -naphthalides, the former crystallising in plates melting at 157—159°, the latter in needles melting at 50°. Small quantities of α -ethoxyisobutyro- β -naphthalido- α -isobutyro- β -naphthalide (m. p. 156—165°) were also obtained. The preceding results show that the isobutyric compounds do not condense to form a diketo-piperazine ring.

L. T. T.

Monoketopiperazines. By C. A. BISCHOFF and C. TRAPESONZJANZ and others (*Ber.*, 25, 2931—2940).—The authors have previously described the diphenyl-, diparatolyl-, and diparaethoxyphenyl-ketopiperazines, which were obtained by heating the secondary bases with chloracetic acid in the presence of dry sodium acetate. Kaminsky has now similarly obtained *di- β -naphthylketopiperazine*,



It crystallises in colourless, hexagonal plates melting at 222—224°. It is sparingly soluble in alcohol, chloroform, acetone, light petroleum, and benzene, insoluble in water and hydrochloric acid. Long-continued boiling with alcoholic potash splits the ring nucleus with formation of the corresponding *acid*, but the acid passes so readily back into the piperazine that it could not be obtained in a state of purity. *Diphenyl- α -keto- β -methylpiperazine*, $\text{NPh} < \begin{array}{c} \text{CH}_2\text{—CH}_2 \\ \text{CO}\cdot\text{CHMe} \end{array} > \text{NPh}$, prepared by Klein, crystallises from benzene in glistening, white, quadratic plates and melts at 137—138°. The corresponding *acid* melts at 83°, and passes into the piperazine at 120° with partial further decomposition. *Diparatolyl- α -keto- β -methylpiperazine* crystallises in flat prisms melting at 117—118°. A second compound, of very similar, if not identical, composition, and most probably a geometric isomeride, was formed at the same time. *Diphenyl- α -ethyl- β -ketopiperazine* crystallises from light petroleum in prisms melting at 93—94°. It is easily soluble in chloroform, carbon bisulphide, benzene, alcohol, and acetic acid. The corresponding *acid* melts at about 40°, and at

120—130° is reconverted into the piperazine. *Diparatolyl- α -ethyl- β -ketopiperazine*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}<\begin{smallmatrix}\text{CH}_2-\text{CH}_2 \\ \text{CHEt}\cdot\text{CO}\end{smallmatrix}>\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$, forms soluble, crystalline aggregates melting at 98—99·5°. The acid is so unstable that it could not be obtained pure. *Diphenyl- α -dimethyl- β -ketopiperazine*, $\text{NPh}<\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2 \\ \text{CMe}_2\cdot\text{CO}\end{smallmatrix}>\text{NPh}$, or possibly



(from α -bromoisobutyric acid), forms thin, colourless plates, crystallising at 116°. Long boiling with alcoholic potash yields the corresponding acid. *Diparatolyl- α -dimethyl- β -ketopiperazine*, $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}$, crystallises in prisms melting at 129—130°. *Diorthotolylketopiperazine* could not be obtained by heating the diamine and bromo-acid with sodium acetate; it was, however, obtained by Walden's method, by reducing the diketopiperazine with tin and fuming hydrochloric acid, or, preferably, with zinc-dust and acetic acid. It crystallises in prisms melting at 79°. *α -Naphthylketopiperazine* was similarly prepared from the corresponding diketopiperazine. It melts at 92°.

The monoketopiperazines are very stable towards nascent hydrogen, the reduction of the more highly oxidised compounds not going beyond the monoketopiperazines.

L. T. T.

Piperazine Group. By C. A. BISCHOFF and others (*Ber.*, 25, 2940—2956).—By the reduction of the derivatives obtained by the action of nitrous acid on the piperazines (*Abstr.*, 1890, 1333), diamido-piperazines are formed. *Diamido-diorthotolylpiperazine*, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}<\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2\end{smallmatrix}>\text{N}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2$, was obtained by Reinus by reducing, by means of tin and hydrochloric acid, the nitration product of diorthotolylpiperazine. It forms intensely yellow, crystalline aggregates melting at 195—196°. It is soluble in alcohol, ether, and benzene, and in dilute acids. *Diamidodiparatolylpiperazine*, similarly prepared by Hoppen, is intensely yellow and crystalline, and melts at 193°. The *hydrochloride* melts at 288—292°; the *sulphate* forms silky needles, darkening at 204—210°, and melting at 217—218°. The base oxidises readily when exposed to the air, especially in the presence of moisture.

Taken in the light of the non-reducibility by nascent hydrogen of the monoketopiperazines (see preceding abstract), the formation of these compounds from the diketopiperazine nitration products proves that, in these latter compounds, the nitration has caused the introduction of the nitro-group into the phenyl nuclei.

No satisfactory results could be obtained by the oxidation of the piperazines, which thus show a marked difference from the ketopiperazines.

Considering the analogy of the piperazines to the hexamethylenes, from which v. Baeyer has obtained geometric isomerides, the former substances were subjected to various modes of treatment, in the hope of producing analogous isomerides. No such geometric isomerides were, however, obtained, but, when heated with a saturated solution of

hydrogen chloride in glacial acetic acid, acetylenediamines were obtained.

Di-α-naphthyl-αβ-diketopiperazine, $C_{10}H_7 \cdot N < \begin{smallmatrix} CH_2 \cdot CH_2 \\ CO - CO \end{smallmatrix} > NC_{10}H_7$,

was prepared by Zabko-Potopowicz from ethylenediphenylamine and oxalic acid. It forms small, colourless plates melting at 281–283°. Potash converts it into the corresponding unstable acid, which gradually passes back into the piperazine at ordinary temperatures, and at once if heated to 127–150°. *Di-β-naphthyl-αβ-diketopiperazine*, prepared by Kochanowski, forms colourless needles melting above 360°. It is soluble in boiling aniline, nitrobenzene, and acetic anhydride, insoluble in most other solvents. At the same time, a small quantity of a yellow powder melting at 200–202° was formed, but it was not further investigated.

Attempts to obtain piperazine derivatives by the action of phosphoric oxychloride on mixtures of anilides and hydroxy-acids proved futile. With tartaric and malic acids, however, closely allied compounds were obtained. From tartaric acid, a compound melting at 234° was formed, which the author believes to be $\begin{smallmatrix} CO - CH \cdot NPh \\ NPh \cdot CH \cdot CO \end{smallmatrix}$, already obtained (Abstr., 1886, 551, 698, 791) from aniline and dibromosuccinic, bromomaleic, or bromofumaric acid. The investigation of this reaction is being continued.

The author also gives a *résumé* of the work done on the piperazine group up to the present.

L. T. T.

Organic Bases in the Juice of Flesh. By G. S. JOHNSON (*Proc. Roy. Soc.*, 50, 287–302). The aqueous extract expressed from the flesh of a healthy cow was treated with mercuric chloride solution, filtered, and the precipitate decomposed by hydrogen sulphide. After filtering, the solution, on spontaneous evaporation over sulphuric acid, deposited *sarcous creatinine hydrochloride* in crystals isomorphous but not identical with those of urinary creatinine hydrochloride. On digesting the aqueous solution of the new salt with lead hydroxide, *sarcous creatinine* is obtained; it forms anhydrous, tabular crystals if prepared in the cold, but, on evaporating its solution at 60°, it separates in efflorescent needles, isomorphous with urinary creatinine. It is soluble in 490·2 parts of alcohol (sp. gr. 0·800) at 13·7°. The *platinochloride*, $(C_4H_7N_3O)_2 \cdot H_2PtCl_6 \cdot 2H_2O$, forms yellow crystals, which lose their water at 100°, and dissolve in 22·6 parts of water at 15°. The *aurochloride*, $C_4H_7N_3O \cdot HAuCl_4$, forms glistening, yellow plates; it is soluble in ether, and the solution, on spontaneous evaporation, deposits a mixture of the hydrochloride and auric chloride. Sarcous creatinine (9 mols.) reduces cupric oxide (4 mols.) in boiling alkaline solution. The properties of this base differ very considerably from those of urinary creatinine.

The excess of mercuric chloride is very slowly, but completely, removed from the mother liquor, remaining after separation of the creatinine compound, by the action of lead hydroxide. From experiments on the amount of creatine contained in the aqueous flesh

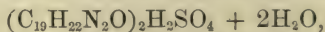
extract, in which germ action was arrested by the addition of mercuric chloride at various periods after death, the author is inclined to conclude that creatine is not originally present in fresh muscle substance, but is a product of bacterial action on some constituent of the flesh; the source of the creatine is probably sarcous creatinine or some closely allied substance. Sarcous creatinine, although probably a true educt, may result from the prolonged action of the mercuric chloride on some similar substance.

Contrary to the general belief, creatine is acted on by mercuric chloride; an aqueous solution of the two substances slowly deposits creatinine mercuric chloride. That this reaction does not occur in treating the flesh extract with mercuric chloride, as described above, is assured by the fact that the creatinine so obtained is not sarcous creatinine, but closely resembles urinary creatinine prepared by Liebig's method.

W. J. P.

Conversion of Cinchona Alkaloids into Isomerides. By Z. H. SKRAUP (*Ber.*, 25, 2909—2912).—Königs has shown (*Abstr.*, 1887, 1123, and 1891, 1010) that when halogen additive derivatives of cinchonine are heated with alcoholic potash, cinchonine is re-formed, together with an isomeride, isocinchonine. The author, working with Pum and Neumann on the hydriodides of various cinchona alkaloids, has found that in many cases little or none of the original alkaloid is re-formed, but that new isomeric bases are produced. This is especially the case when the decomposition of the halogen derivative is effected by means of silver nitrate in place of alcoholic potash. Cinchonide hydriodide yields with alcoholic potash β -cinchonidine, melting at 244° ; its *sulphate*, *hydrochloride*, and *nitrate* are non-crystallisable, whilst its *oxalate* and *normal tartrate* are crystalline. In other respects it closely resembles cinchonidine. With silver nitrate, on the other hand, cinchonidine hydriodide yields γ -cinchonidine, melting at 238° , and giving salts of which only the *acid tartrate* is crystallisable.

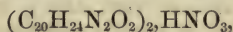
Cinchonine hydriodide treated with silver nitrate yields some isocinchonine, but mainly β -cinchonine, sparingly soluble in ether, melting at 250 — 252° , and giving a characteristic *sulphate*,



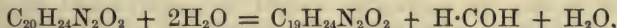
crystallising in matted needles. Isocinchonine and β -cinchonine give hydriodides, which in physical properties both closely resemble that of cinchonine. But the β -hydriodide, when treated either with alcoholic potash or silver nitrate, yields β -cinchonidine, with only very little isocinchonine, whilst the iso-hydriodide yields with potash only very little isocinchonine, a new isomeride, γ -cinchonine, being the chief product. This melts at 230 — 235° , and gives an anhydrous *sulphate* $(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O})_2\text{H}_2\text{SO}_4$, crystallising in needles. It is possible that these β - and γ -cinchonines may be identical with the alkaloids obtained by Jungfleisch and Leger by heating cinchonine with sulphuric acid.

When quinine hydriodide is heated with alcoholic potash, about equal proportions of quinine, *pseudoquinine*, and *nichine* are produced. If silver nitrate is used in place of potash, the same products are formed, but *nichine* predominates. *Pseudoquinine*, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$, crystal-

lises easily, melts at 191° , and is lævorotatory. The *hydrochloride*, $C_{20}H_{24}N_2O_2 \cdot HCl$, the *normal nitrate*, and a *basic nitrate*,



are sparingly soluble and crystallise easily. *Nichine*, $C_{19}H_{24}N_2O_2$ (or, possibly, $C_{19}H_{22}N_2O_2$), crystallises easily and yields well crystallised *acid hydrochloride*, *hydriodide*, and *sulphate* sparingly soluble in alcohol and water, and an *oxalate* (with 2 mols. oxalic acid), almost insoluble in boiling alcohol. The formation of nichine probably takes place according to the reaction



and an aldehydic compound was found to be present in the products of reaction.

With hydriodic acid, pseudoquinine yields a hydriodide, probably identical with that formed from quinine. Nichine forms a *hydriodide*, $C_{19}H_{24}N_2O_2 \cdot 3HI$, differing entirely from the corresponding derivative of quinine. When decomposed by alcoholic potash, it yields mainly regenerated nichine, together with a little of a new isomeride, *isonichine*. The authors believe Lippmann and Fleissner's isoquinine (Abstr., 1892, 82) was a mixture of pseudoquinine and nichine.

An aldehydic substance reducing silver nitrate was also found in the distillates from the decomposition of the hydriodides of cinchonidine, and it is, therefore, possible that alkaloids containing one less carbon atom than the originals were also formed in these reactions. (Compare also Abstr., 1891, 1517; 1892, 83, 640, and 1363.)

L. T. T.

Coca Leaves. By O. HESSE (*Annalen*, **271**, 180—228).—In this paper, the author gives a short account of the various substances which have been obtained from coca leaves; with a few exceptions, most of the compounds here referred to have been previously described by the author (Abstr., 1889, 751, and *Pharm. J. Trans.* [3], **21**, 1109, 1120); Liebermann (Abstr., 1890, 76, 494; 1891, 1265, 1520); Einhorn, Giesel, and others.

Cinnamylcocaine hydrochloride, $C_{19}H_{23}NO_4 \cdot HCl + 2H_2O$, crystallises from water, in which it is readily soluble, in lustrous plates, loses its water at 66° , and melts at 176° ; its specific rotatory power in aqueous solution is $[\alpha]_D = -104.1$. The *platinochloride*, $(C_{19}H_{23}NO_4)_2 \cdot H_2PtCl_6$, crystallises in small needles, and is moderately easily soluble in boiling water. The *aurochloride*, $C_{19}H_{23}NO_4 \cdot HAuCl_4$, crystallises in small, yellow needles, and melts at 156° . The *methiodide*, $C_{19}H_{23}NO_4 \cdot MeI$, crystallises from alcohol in small, colourless needles; the corresponding *methochloride* is a crystalline substance, readily soluble in water and alcohol, but insoluble in ether.

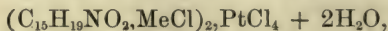
The molecular formula of homococaïc acid, determined in glacial acetic acid solution, was found to be $C_9H_9O_2$. This acid melts at 150° , and dissolves freely in alcohol, ether, chloroform, glacial acetic acid, and hot water, but is only sparingly soluble in light petroleum and cold water; it is only slowly oxidised by a warm solution of potassium permanganate. A number of its salts were prepared and analysed.

but they are all amorphous, ill-characterised compounds. The *nitro*-derivative, $C_9H_7O_2 \cdot NO_2$, prepared by warming the acid with nitric acid of sp. gr. 1.52, crystallises from dilute acetic acid in yellowish needles, melts at 226° , and is readily soluble in alcohol and glacial acetic acid, but more sparingly in chloroform, ether, and boiling water.

β -Cocaïc acid, $C_{18}H_{16}O_4$, is formed when homococaïc acid is heated for a long time with concentrated hydrochloric acid, or fused with potash; it crystallises from boiling water in long, colourless needles, melts at 189° , and is readily soluble in glacial acetic acid, alcohol, and chloroform, but more sparingly in benzene, and almost insoluble in light petroleum; its molecular weight was determined in glacial acetic acid solution, with results in accordance with the molecular formula given above. It is only very slightly acted on by potassium permanganate. The *potassium* salt crystallises in lustrous prisms, and is readily soluble in cold water. The *copper* salt, $C_{18}H_{14}O_4Cu + 2H_2O$, is a green, crystalline compound, and loses its water at 160° , becoming dark-blue. The *silver* salt, $C_{18}H_{14}O_4Ag_2$, is stable in the light. The *methyl* salt, $C_{18}H_{14}O_4Me_2$, is a mobile oil. The *dinitro*-derivative, $C_{18}H_{14}O_4(NO_2)_2$, prepared by treating the acid with concentrated nitric acid, crystallises from glacial acetic acid in pale yellow prisms, melts at 252° , and is readily soluble in alcohol, chloroform, glacial acetic acid, and ether, but more sparingly in water.

β -Isococaïc acid or δ -truxillic acid (compare Liebermann, Abstr., 1889, 1194), prepared from isococaïc acid in like manner, has the molecular formula $C_{18}H_{16}O_4$; it melts at 172° , not at 174° , as stated by Liebermann. The *barium* salt, $C_{18}H_{14}O_4Ba + 4H_2O$, crystallises in short, lustrous prisms; the *copper* salt crystallises with 2 mols. H_2O . The *dinitro*-derivative, $C_{18}H_{14}O_4(NO_2)_2$, crystallises from dilute acetic acid in small, almost colourless prisms, melts at 226° , and is very readily soluble in alcohol and ether, but almost insoluble in benzene.

Benzoylpseudotropéine methiodide, $C_{15}H_{19}NO_2 \cdot MeI$, forms colourless crystals, and is moderately easily soluble in hot, but only sparingly in cold, alcohol. The corresponding *methochloride*, $C_{15}H_{19}NO_2 \cdot MeCl$, crystallises in colourless needles or prisms; its *platinochloride*,



forms small, orange needles, and is sparingly soluble in cold water; its *aurochloride*, $C_{15}H_{19}NO_2 \cdot MeCl \cdot AuCl_3$, is a yellow, crystalline compound, sparingly soluble in cold water.

Pseudotropéine methiodide, $C_8H_{15}NO \cdot MeI$, crystallises from hot water in small, colourless, rhombic crystals, and melts at 270° . The *methochloride*, $C_8H_{15}NO \cdot MeCl$, forms compact, rhombic crystals, and is readily soluble in water, but only sparingly in alcohol; its *platinochloride*, $(C_8H_{15}NO \cdot MeCl)_2 \cdot PtCl_4$, separates from hot water in crystals, and melts at 216° .

Palmityl- β -amyrin, $C_{46}H_{80}O_2$, occurs in Trujillo coca; it melts at 75° , dissolves freely in ether, chloroform, light petroleum, hot alcohol, and acetone, and has a specific rotatory power $[\alpha]_D = 54.5^\circ$ in alcoholic solution; on hydrolysis, it yields palmitic acid and β -amyrin. The wax obtained from the broad-leaved coca of Peru and Bolivia consists of palmityl- β -amyrin and cerotone, $C_{53}H_{106}O$, melting at 66° ; the wax

from Java coca seems to consist of palmityl- β -amyrin, cerotone, ceryl cerotate, myristyl- β -amyrin, and a substance which the author names hydroxycerotic acid.

Hydroxycerotic acid, $C_{27}H_{54}O_3$, melts at 82° , and dissolves freely in hot alcohol and light petroleum, but is only very sparingly soluble in cold ether.

Cerotic acid, $C_{27}H_{52}O_2$, is formed when hydroxycerotic acid is heated at 100° with acetic anhydride for eight days; it crystallises in short prisms, and is moderately easily soluble in cold ether and light petroleum. F. S. K.

Echinochrome, a Respiratory Pigment. By A. B. GRIFFITHS (*Compt. rend.*, 115, 419—420).—The echinochrome discovered by MacMunn in several echinoderms is a respiratory pigment existing in two states of oxidation. It has the empirical composition $C_{102}H_{99}N_{12}FeS_2O_{12}$, is partially soluble in water or alcohol, and dissolves readily in chloroform, benzene, or carbon bisulphide. When boiled with inorganic acids, it yields hæmatoporphyrin, hæmochromogen, and sulphuric acid.

Echinochrome in some respects is analogous to hæmoglobin and chlorocruorin, and is probably a respiratory pigment in a low state of development. The respiratory pigments of the lower animals not only carry oxygen to the tissues, but also retain oxygen until they are themselves taken up by the tissues in the processes of metabolism. This is why hæmocyannin, chlorocruorin, pinnaglobin, achroglabin, and echinochrome are much more stable than hæmoglobin.

C. H. B.

Hermerythrin, a Respiratory Pigment contained in the Blood of certain Worms. By A. B. GRIFFITHS (*Compt. rend.*, 115, 669—670).—Hermerythrin, described by Krøkenberg, was extracted from the blood of *Sipunculus* and analysed. The results lead to the empirical formula $C_{427}H_{761}N_{135}FeS_2O_{153}$. The pigment exists in two states, oxyhermerythrin, which is red, and reduced hermerythrin, which is brown. The ash of the blood of *Sipunculus* has the composition: Fe_2O_3 , 0.13; CaO , 3.00; MgO , 1.65; K_2O , 5.02; Na_2O , 44.31; P_2O_5 , 4.78; SO_3 , 2.86; Cl , 38.25.

C. H. B.

Fractional Heat Coagulation. By R. T. HEWLETT (*J. Physiol.*, 13, 493—512).—In determining the coagulation temperatures of proteïds, an oil-bath has some advantages over a water-bath. There is no need to make a distinction between temperature of opalescence and temperature of coagulation (formation of flocculi). Both take place at the same temperature if the rate of heating is sufficiently slow. A slow rate of heating is essential for obtaining correct coagulation temperatures, especially when the solution is dilute. Prolonged heating does not alter the coagulation temperature of a proteïd. Very dilute solutions of a proteïd may be prevented from coagulating by a comparatively small excess of acid or alkali. The phenomena of fractional heat coagulation are not due, as Haycraft and Duggan state, to the effects of dilution for (a) dilution, if the rate of heating be

sufficiently slow, does not raise the coagulation temperature, and (b) in fractionating, the rise in the coagulation temperature is out of all proportion to the dilution. A striking experiment confirmatory of the foregoing was the following: white of egg solution was heated to the temperature at which coagulation first occurred; this was filtered off; the filtrate coagulated at a higher temperature, showing the presence of a second proteid with a higher coagulation temperature, as Halliburton would say; this view was confirmed by concentrating the filtrate, and thus dilution of the solution was obviated. The filtrate, however, still coagulated at the higher temperature, although its concentration was, so far as proteid in it was concerned, as great as in the original liquid.

White of egg is a mixture of at least three proteids, one of which is a globulin coagulating at 56°.

The opinion is expressed that it would be advisable to decide on some standard conditions (solvent, &c.) under which to determine coagulation temperatures.

W. D. H.

Rotatory Power of Fibroïn. By L. VIGNON (*Compt. rend.*, 115, 442—444).—The author has already shown that an acid solution of fibroïn from silk acts on polarised light (*Abstr.*, 1892, 254, 265). If a solution of fibroïn in hydrochloric acid is gradually neutralised with sodium hydroxide, an abundant, white precipitate is formed near the point of neutrality, but precipitation is never complete. The precipitate, when freshly prepared, is soluble in sodium hydroxide.

If, however, 20 c.c. of the hydrochloric acid solution of fibroïn is mixed with 100 c.c. of ethyl alcohol of 95°, the fibroïn is completely precipitated without alteration of properties. When dried by exposure to air, its sp. gr. is 1.32, and it is insoluble in cold dilute sodium hydroxide solution, but dissolves in concentrated hydrochloric acid, and is decomposed by warm concentrated sodium hydroxide solution. The precipitated fibroïn has a rotatory power $[\alpha]_D = -43.2^\circ$, practically identical with that of the original fibroïn, and it exerts the same absorptive action on colouring matters.

C. H. B.

Respiratory Globulin in the Blood of Chitons. By A. B. GRIFFITHS (*Compt. rend.*, 115, 474—475).—The blood of chitons has a yellow colour, but the pigment is a lutein or lipochrome, and has no respiratory function. The blood, however, contains a colourless respiratory globulin with the same function as hæmoglobin, hæmocyanin, pinnaglobin, and chlorocruorin, but it contains no metal. Its empirical formula is $C_{621}H_{814}N_{175}SO_{169}$, and 100 c.c. absorb 120 c.c. of oxygen and 281 c.c. of carbonic anhydride at 0° and 760 mm. When dissolved in a dilute solution of magnesium sulphate, its specific rotatory power $[\alpha]_D = -55^\circ$. Even when oxygenated, it is colourless, and the author calls it β -achroglobin in order to distinguish it from achroglobin, which exists in the blood of *Patella*.

C. H. B.

Organic Chemistry.

Hydration of Ethylenic Hydrocarbons. By S. MIKLASHEFFSKY (*J. Russ. Chem. Soc.*, **22**, 495—506).—As very dilute solutions of mineral acids can bring about the addition of the elements of water to unsaturated hydrocarbons of the ethylene series, the author has investigated the capability of the feeble organic acids to effect the same addition. He employed, principally, solutions of oxalic acid of 5, 8, and 10 per cent. concentration.

Isobutylene prepared from isobutyl iodide was led into soda water bottles containing the acid solution, and immersed in a freezing mixture. When a sufficient quantity of the hydrocarbon had condensed, the bottles were closed by an india-rubber stopper tied firmly down, and were then left lying in a horizontal position, some at the ordinary temperature, and some at about 40°. After the lapse of a month, it was found that the layer of hydrocarbon had completely disappeared in the bottles which had been heated. These were then opened, their contents neutralised with potassium carbonate, and the colourless oil which separated, distilled off on the water-bath. This oil, when dried with fused potash and boiled with baryta, distilled at 82·5—83°, solidifying in the receiver to prismatic crystals, which melted at about 25°. From these data, and the strong camphoric odour of the substance, it would appear to be trimethylcarbinol. The same reaction occurs at the ordinary temperature, but the time required for its completion is about two and a half months.

Commercial amylene is very slowly attacked at the ordinary temperature by solutions of oxalic acid, but at 100°, the addition of water goes on more rapidly, a considerable quantity of the hydrocarbon disappearing after four days' heating. The aqueous solution was found to contain dimethylethylcarbinol, boiling at 101·5°. At the ordinary temperature, the same substance was formed in the course of a year. Experiments with similar results were also made on the mixture of the two isomeric amylenes, prepared by the action of alcoholic potash on dimethylethylcarbinyl iodide. The alcohol thus prepared has a sp. gr. = 0·8268 at 0°/0°, and 0·8103 at 21·5°/21·5°. The corresponding chloride boiled at 86—87°. Acetic and formic acids behave similarly to oxalic acid, only their action is much slower, acetic acid being the least active of the three.

Normal propylethylene did not take up the elements of water under the above conditions.

On heating tetramethylethylene from the iodide of dimethylisopropylcarbinol with the acid for 2—3 weeks at 100°, it gave the original alcohol boiling at 117—119° under a pressure of 765 mm.

Diisobutylene remained unchanged on similar treatment.

The organic acids are thus active in effecting the conversion of unsaturated hydrocarbons into tertiary alcohols precisely in the same way as the strong mineral acids, from which they differ, however, in not simultaneously causing polymerisation of the hydrocarbons.

J. W.

Preparation of Acetylene. By L. MAQUENNE (*Compt. rend.*, 115, 558—561).—Barium carbide is easily obtained in large quantities and in a pure condition in the following manner. 26 grams of precipitated barium carbonate is mixed with 10.5 grams of powdered magnesium and 4 grams of retort carbon previously heated in a platinum crucible, and the mixture is placed in an iron bottle of about 700 c.c. capacity, to the neck of which is fitted an iron tube 30 cm. long and 2 cm. in diameter; on heating the bottle to redness, an energetic reaction soon takes place, with projection of sparks from the end of the tube. When this ceases, the end of the tube is closed, and the bottle is cooled as rapidly as possible. The product is a mixture of magnesium oxide with 38 per cent. of barium carbide, a small excess of carbon, and a trace of cyanide. It is a light, porous, friable, amorphous mass of a grey colour. It does not alter in dry air, and is not attacked by chlorine or gaseous hydrogen chloride in the cold. Acid anhydrides, acid chlorides, and even phosphorus pentachloride, have no action on it at 100°; at a red heat, it burns with vivid incandescence in air, sulphur vapour, chlorine, or hydrogen chloride.

When treated with water, alcohol, or, as a rule, any compound containing hydroxyl, barium carbide yields acetylene at the ordinary temperature. If water is allowed to fall on the carbide drop by drop, a regular current of acetylene is obtained containing only 2 to 3 per cent. of hydrogen, and no appreciable trace of any other hydrocarbon, the yield being about two-thirds of that calculated from the weight of magnesium originally employed.

By passing this acetylene through a long glass tube heated to dull redness, the author has obtained in one day several grams of synthetic benzene.

C. H. B.

Action of Bromine on Ethyl Chloride and on certain Butane Derivatives. By V. MEYER and P. PETRENKO-KRITSCHENKO (*Ber.*, 25, 3304—3310; compare Meyer and Müller, *Abstr.*, 1892, 1414).—Ethyl chloride is heated on the water-bath in a sealed tube with iron wire and bromine; the product consists of ethylene bromide (66 per cent.) and ethyl bromide (14.5 per cent.); the chlorine is, therefore, displaced by the bromine, and the ethyl bromide then undergoes further substitution in the usual manner.

By the action of bromine on butyl bromide, Meyer and Müller obtained (*loc. cit.*) a compound which they believed to be pseudo-butylene bromide, $\text{CHBrMe} \cdot \text{CHBrMe}$; on heating it with lead oxide and water in a sealed tube at 150°, ethyl methyl ketone is formed, and their supposition is thus shown to be correct. It is probable that in the process of bromination, normal butyl bromide is converted into secondary butyl bromide.

1:1-Dichlorobutane, prepared from phosphoric chloride and normal butaldehyde, is also decomposed by the action of water and lead oxide, butaldehyde being regenerated.

J. B. T.

Catalytic Action of Aluminium Chloride on Ethereal Silicates. By H. N. STOKES (*Amer. Chem. J.*, 14, 438—454).—Aluminium chloride dissolves quietly in ice-cold ethyl trichlorosilicate,

$\text{SiCl}_3\cdot\text{OEt}$, but on allowing the temperature to rise, a violent reaction sets in, and ethyl chloride is evolved. The aluminium chloride, of which a trace is enough to determine the reaction, may afterwards be distilled unchanged from the residue, which has the approximate composition SiOCl_2 , although it is probably a complex mixture of silica with various oxychlorides of silicon. It is possible that unstable intermediate compounds such as $\text{SiO} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \end{smallmatrix} \text{AlCl}$ and $\text{Cl}_2\text{AlO}\cdot\text{SiO}\cdot\text{OAlCl}_2$, of gradually increasing complexity, are formed by the assumption of aluminium chloride, rearrangement of the complex, and elimination of the chlorine, and a number of equations are given in illustration of this view, which is borne out, moreover, by the gradual increase in viscosity of the liquid during the course of the reaction. The rearrangement may be attributed to the superior affinity of silicon over that of aluminium for oxygen. Further evidence in favour of the existence of complex aluminium chlorosilicates and silicon oxychlorides is furnished by the interaction of aluminium chloride with ethyl monochlorosilicate. The silicate, like its trichlorinated analogue, is completely decomposed under the influence of a very small quantity of the chloride, ethyl chloride and ether being formed, but the aluminium chloride remains combined with the silica, since, as the hypothesis points out, there is not enough chlorine in the silicate to complete the regeneration. But as the proportion of aluminium chloride increases, less ether is formed and more ethyl chloride, and when the ratio of silicon to aluminium is as 3 : 2, the whole of the chlorine passes into the ethyl chloride, and no ether is formed at all. Any excess of the chloride over this amount may be sublimed unchanged at the end of the operation. With ethyl orthosilicate, the reaction is of a different character. Since there is no chlorine in it, there is no regeneration of aluminium chloride, and hence the amount of change is strictly proportional to the amount of the latter. The formation of ether is probably due to the breaking-down of intermediate ortho-compounds such as $(\text{EtO})_2\text{SiO}_2\text{AlCl}$, the ortho-acids of silicon, like those of carbon, seeming to rise to their highest basicity only in their ethereal combinations.

JN. W.

Alcohols in Fusel Oil. By R. C. SCHÜPPHAUS (*Chem. Centr.*, 1892, ii, 206; from *J. Amer. Chem. Soc.*, 14, 45—60).—In order to analyse fusel oil, it must be completely dried with anhydrous potassium carbonate, and then repeatedly fractionated. In four samples were found water, 14—23; normal propyl alcohol, 5·7—14·5; isobutyl alcohol, 11·0—25·2; fermentation amyl alcohol, 7·0—36·8; residue, boiling above 132° , probably a mixture of amyl ethers, 0·5—2·0 parts per cent. Rabuteau's statement that isopropyl alcohol is contained in fusel oil is probably incorrect.

C. F. B.

Levulan. By E. O. v. LIPPMANN and O. HAHN (*Ber.*, 25, 3216).—The authors, having obtained another sample of levulan, have repeated Lippmann's experiments on its oxidation with nitric acid. They find that no mucic acid is formed, oxalic acid being the chief product. Its behaviour on oxidation is, therefore, in consonance with its close relationship to levulose.

L. T. T.

Dulcitol. By E. O. v. LIPPMANN (*Ber.*, **25**, 3216—3218).—The author has obtained dulcitol from the products of the yeast fermentation of a Mozambique cane sugar. During his work on this subject, he observed a peculiar mucous fermentation in a sample of calcium mucate, pyrrolone being found amongst the products. L. T. T.

Sorbitol. By E. O. v. LIPPMANN (*Ber.*, **25**, 3218—3220).—The author has discovered small quantities of sorbitol in a sample of molasses from mixed sugars of various sources. L. T. T.

Agavose. By G. MICHAUD and J. F. TRISTAN (*Amer. Chem. J.*, **14**, 548—550).—The *Agave Americana* is extensively grown in Mexico for the sake of the juice of the stalk, from which a fermented intoxicating drink called *pulque* is made. The substance yielding the alcohol is a sugar, which may be isolated by the following process:—The juice is first treated with alcohol (2 vols. 90 per cent.) and filtered; basic lead acetate is next added to the solution, which is again filtered, the excess of lead being subsequently removed from the filtrate by means of hydrogen sulphide; the clear liquid is now evaporated to a syrup under diminished pressure, and left to crystallise in a warm place.

Agavose, $C_{12}H_{22}O_{11}$, is an inactive sugar, which reduces alkaline copper tartrate, and yields a lævoglyrate sugar ($[\alpha]_D = -14.43$) on inversion. It is oxidised by nitric acid, but not to mucic acid, and forms a soluble lime compound, which is precipitated by alcohol or by heating.

JN. W.

Effect of Boiling with Water on Cane Sugar and Raffinose.

By J. WEISBERG (*Chem. Centr.*, 1892, ii, 458; from *Österr.-ungar. Zeit. Zuck.-Ind. Landw.*, **21**, 438—442).—An aqueous solution of pure cane sugar may be heated for an hour at 100—105° without any change taking place. After heating for several hours, a slight decrease of rotatory power can be observed, and the solution reduces Fehling's solution to some extent. The same is the case if the sugar solution is made alkaline and traces of inorganic or organic salts added, or if lime is present.

Raffinose is even less affected than cane sugar; the boiling with water must be continued for 15 hours before any decrease of rotatory power can be detected, and even then there is hardly any apparent reduction of Fehling's solution. C. F. B.

Metaldehyde and Paraldehyde. By J. TROEGER (*Ber.*, **25**, 3316—3317).—A sample of pure metaldehyde which had been kept for 10 years protected from direct sunlight was found to have undergone partial conversion into acetaldehyde and paraldehyde, the latter predominating. A conversion of paraldehyde into acetaldehyde under like circumstances was also observed. A. R. L.

Thiocyanacetone. By A. HANTZSCH (*Ber.*, **25**, 3282—3286).—A refutation of Tcherniac's criticisms (*Abstr.*, 1892, 1425).

Substitution in Aliphatic Acids. By V. MEYER (*Ber.*, **25**, 3310—3312).—The author refers to the fact that α -halogenated

fatty acids are always obtained by direct substitution, and that this process was believed to be analogous to the formation of di-halogenated substituted paraffin derivatives, thus: $\text{CHMe}\cdot\text{COOH}$ and CH_2MeCl gave $\text{CHMeCl}\cdot\text{COOH}$ and CHMeCl_2 respectively. It has, however, been shown by the author and Müller that in the case of paraffin hydrocarbons the second halogen atom links itself to the carbon atom adjacent to that to which the first halogen atom is linked; but the analogy in the substitution of the two classes of compounds is still maintained, as is readily perceived from a comparison of the substituted acid chlorides and substituted hydrocarbons:— $\text{CH}_3\cdot\text{CH}_2\text{Cl}$ and $\text{CH}_3\cdot\text{COCl}$ give $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Cl}$ and $\text{CH}_2\text{Cl}\cdot\text{COCl}$; $\text{CH}_2\text{Me}\cdot\text{CH}_2\text{Cl}$ and $\text{CH}_2\text{Me}\cdot\text{COCl}$ give $\text{CHMeCl}\cdot\text{CH}_2\text{Cl}$ and $\text{CHMeCl}\cdot\text{COCl}$ respectively; the hydroxyl group in the acids is, therefore, the negative group, and plays the same part as the chlorine atom in the substituted hydrocarbons.

J. B. T.

Method of preparing Brominated Fatty Acids. By P. GENVRESSE (*Bull. Soc. Chim.* [3], 7, 364—366).—Auger and Béhal (Abstr., 1890, 234) have prepared monochloracetic acid by passing chlorine into boiling glacial acetic acid in the presence of sulphur.

An almost theoretical yield of monobromacetic acid is obtained by gradually adding rather more than the calculated quantity of bromine to a mixture of boiling glacial acetic acid with 5 per cent. of sulphur; the flask containing the mixture should be fitted with a reflux condenser, having a wide tube. Dibromacetic acid is prepared by continuing the addition of bromine to the monobromo-derivative, which may be kept at about 150° . α -Bromopropionic acid is prepared in the same manner (compare Lepercq, next abstract), as is also α -bromobutyric acid.

A. R. L.

Action of Alkali Nitrites on Alkyl Salts of Brominated Fatty Acids. By G. LEPERCQ (*Bull. Soc. Chim.* [3], 7, 359—361).—Steiner has shown that when a mixture of ethyl chloracetate and potassium nitrite is gently heated, gaseous products and potassium ethyl oxalate are formed; the author states that a nitrogenous compound is also produced.

α -Bromopropionic acid is first prepared by gently heating a mixture of propionic acid (125 grams), bromine (310 grams), and sulphur (2.5 grams) in a reflux apparatus for two hours (compare preceding abstract), and is then converted into the ethyl salt by dissolving it in absolute alcohol, and heating the solution with 5 per cent. of sulphuric acid in a reflux apparatus for two hours. When ethyl α -bromopropionate is heated on the water-bath with its own weight of alcohol and sodium nitrite (2 mols.), hydrogen cyanide, nitrogen, carbonic anhydride, and a little nitric oxide are evolved. The alcoholic liquid is filtered, evaporated on the water-bath, and the residue poured into water, when a red liquid, which cannot be distilled even under diminished pressure, is precipitated, whilst on evaporating the aqueous portion, in a partial vacuum, a compound crystallising in needles is isolated. Both substances contain nitrogen, and are under investigation. Ethyl α -bromobutyrate reacts in like manner with sodium nitrite.

A. R. L.

Ethyl Acetoacetate and Ethyl Salicylate. By P. C. FREER (*Amer. Chem. J.*, **14**, 407—422; compare Abstr., 1891, 1181).—The author controverts the conclusion which Nef (Abstr., 1892, 140) draws from the observation that an additive product is formed previous to the separation of the sodium halide in the action of alkyl halides on ethyl acetoacetate. If ethyl acetoacetate is, in reality, ethyl β -hydroxycrotonate, as Nef contends, it contains the same grouping as ethyl salicylate, and the sodium compound of the latter should, therefore, form similar additive compounds. But it does not do so, for the substituting radicle is united to the molecule by oxygen, as is proved by the readiness with which it is removed by hydrolysis. The action of phenylhydrazine hydrochloride on ethyl acetoacetate gives rise to phenylmethylpyrazolone, and also a substance melting at 36° which is identical with that obtained by Nef by the action of acetic chloride on ethyl β -phenylhydrazocrotonate. Ethyl acetoacetate does not yield an acetyl derivative, whilst its analogue, ethyl salicylate, does so readily.

Ethyl sodiosalicylate is prepared by adding either powdered sodium to the toluene solution, or aqueous sodium hydroxide to the ethereal solution of ethyl salicylate; it is a white solid, which is soluble in water with partial decomposition. When bromine is added to an ethereal solution of this substance, a dibromo-substitution product and ethyl salicylate are simultaneously formed, the bromine replacing hydrogen and liberating hydrogen bromide, and the latter then decomposing a further quantity of the substance.

Ethyl dibromosalicylate crystallises from alcohol in nacreous plates, and melts at 100 — 101° . It is sparingly soluble in hot or cold water, but easily in alkalis. By heating with alcoholic potash, and subsequently treating with dilute sulphuric acid, it is converted into *dibromosalicylic acid*, which crystallises from dilute alcohol in white needles, and melts at 225° . Ethyl dibromosalicylate is reduced to salicylic acid by sodium amalgam in boiling dilute alcoholic solution. When ethyl salicylate is treated with bromine in chloroform solution, *ethyl metabromosalicylate* is formed; it crystallises from alcohol in long needles, and melts at 49 — 50° . The corresponding acid crystallises from dilute alcohol in colourless needles, melts at 165 — 166° , and is apparently identical with the metabromosalicylic acid of Hübner and Heinzenberg (*Zeit. Chem.*, 1871, 709).

Ethyl benzoylsalicylate is prepared by treating dry ethyl sodiosalicylate with excess of benzoic chloride. It crystallises from dilute alcohol in small, flaky plates, and melts at 79 — 80° . It is decomposed into benzoic and salicylic acids by alcoholic potash, showing that the benzoyl radicle is attached to oxygen.

Ethyl diethylsalicylate is formed by treating ethyl sodiosalicylate with ethyl iodide in alcoholic solution. It is a colourless oil which boils at 252° , and yields diethylsalicylic acid on boiling with alcoholic potash. The corresponding methyl compounds agreed with those described by Graebe (*Annalen*, **139**, 137). *Ethyl cuprosalicylate*, prepared by treating alcoholic ethyl sodiosalicylate with copper acetate, like ethyl cupracetoacetate, does not react with alkyl iodides. *Ethyl acetylsalicylate* is prepared by boiling ethyl salicylate with acetic

chloride for some hours in a reflux apparatus. The product is poured into ice-cold water, extracted with ether, the ethereal solution washed with concentrated alkali to separate unchanged ethyl salicylate, and dried over calcium chloride. On evaporating the ether, the acetyl salicylate remains as a thick, colourless oil, which boils at 273° , and is readily decomposed by alcoholic potash.

The products of the action of phenylhydrazine hydrochloride on ethyl acetoacetate are, firstly, phenylmethylpyrazolone, and, secondly, a white, amorphous solid, which melts at 36° , as stated above, and appears to have the composition $C_{12}H_{14}N_2O$. It is soluble in alcohol, chloroform, and ether, but insoluble in cold water and alkalis, and is identical with the oil obtained by Nef (*loc. cit.*) by the action of acetic chloride on ethyl β -phenylhydrazocrotonate, and prepared by the author by the action of acetic chloride on the phenylhydrazine of ethyl acetoacetate. It is not affected by alkalis and concentrated sulphuric acid, and when treated with bromine in chloroform solution, forms a dibromo-additive product, which crystallises in large, colourless prisms, and melts at $111-112^{\circ}$. When treated with methyl iodide, it yields a syrup resembling that obtained in a similar manner from phenylmethylpyrazolone, and is, therefore, probably similar in constitution.

Ethyl acetoacetate is completely decomposed by hydrogen bromide into ethyl bromide, alcohol, ethyl acetate and acetone. If an additive product is formed, which is doubtful, it is very unstable in character.

JN. W.

Ethyl Sodacetoacetate. By A. MICHAEL (*Amer. Chem. J.*, **14**, 481—544; compare Abstr., 1892, 1178 and 1428).—The product of the action of ethyl chlorocarbonate on ethyl sodacetoacetate is not the acid substance ethyl acetomalonate, for which it was mistaken by Conrad and Guthzeit (*Annalen*, **214**, 31), although they could not succeed in displacing any of the hydrogen by sodium, but a neutral substance, which is resolved into ethyl sodacetoacetate and ethyl carbonate by sodium ethoxide, and has, therefore, the constitution $COOEt \cdot O \cdot CMe \cdot CH \cdot COOEt$ (compare Nef, Abstr., 1892, 140). The formation of this compound confirms the view that the sodium in ethyl sodacetoacetate is attached to oxygen and not directly to carbon. There is no reason, however, for attributing a carbinol constitution to ethyl acetoacetate, and its reactions are best explained by means of the ketone formula. The fact that the alkyl and similar groups in the substitution products of ethyl acetoacetate are undoubtedly attached to the methylene carbon, may be explained by assuming the transient existence of an unstable intermediate additive compound, such as $ONa \cdot CMe \cdot CH \cdot COOEt$, which is formed in consequence of the attraction of the negative iodine of the ethyl iodide for the relatively positive sodoxyl carbon, and of the positive ethyl for the relatively negative methine carbon. As soon, however, as the negative iodine comes within the sphere of influence of the positive sodium, sodium iodide is formed, and the carbon sodoxyl reverts to carbonyl. Nef's hypothesis (*loc. cit.*) that the additive compound is decomposed by the elimination of hydrogen iodide, the hydrogen

of which afterwards replaces the sodium, seems untenable. His contention, too, that acetoacetanilide is an unsaturated substance, because it unites with bromine to form an unstable additive compound, is unsound, since acetic acid itself forms a similar, but much more stable, compound. The formation of the ketonic ethyl acetoacetate from the carbinolic ethyl sodacetoacetate, and *vice versa*, may be regarded as instances of *merotropy*, or molecular rearrangement due to alteration of stability of the molecule by the introduction or substitution of a foreign atom. When ethyl sodacetoacetate, for instance, is treated with water, it may be assumed that the hydrogen takes the place of the sodium in the first instance, but that the compound so formed, like all other compounds having hydroxyl and hydrogen linked to adjacent unsaturated carbon atoms (hydroxyethylene, for example), is very unstable, and passes at once into the ketonic form by shifting of the hydrogen atom. The hydroxy-compound has thus no separate existence. In the reverse case, when ethyl acetoacetate is acted on by sodium, one of the methylene hydrogen atoms is displaced by the metal, but the compound thus formed at once passes into the carbinol form, owing to the attraction of the negative carbonyl oxygen for the positive sodium. Thus, neither ethyl acetoacetate nor its sodium derivative can be said to have two structures; these, and all other compounds, assume the most stable structure consistent with their composition, and if the composition is altered by the introduction or substitution of foreign atoms, the former structure may be thrown out of balance, and another more stable assumed. All the known phenomena of tautomerism and desmotropy may be explained in terms of this conception of merotropy, in conjunction with the "positive-negative" hypothesis mentioned above.

Ethyl carbethoxyacetoacetate, $\text{COOEt} \cdot \text{OCMe} : \text{CH} \cdot \text{COOEt}$, is prepared by adding ethyl chlorocarbonate gradually to an ice-cold ethereal suspension of ethyl sodacetoacetate. A small amount, at the most 10 per cent., of ethyl acetomalonate is formed at the same time, and may be dissolved out by dilute aqueous soda. Ethyl carbethoxyacetoacetate boils without decomposition at 136° under 20 mm. pressure (133° under 17 mm.). Its vapour density corresponds with the constitution given above, and not with that of ethyl acetomethanetricarboxylate, as proposed by Nef (*loc. cit.*). It is neutral, moreover, towards alkalis. When dry powdered sodium ethoxide is gradually added to ice-cold ethyl carbethoxyacetoacetate, ethyl carbonate and sodacetoacetate are formed. When an aqueous solution of phenylhydrazine and sodium acetate is added to an alcoholic solution of ethyl carbethoxyacetoacetate (10 grams), phenylmethylpyrazolone and ethyl phenylhydrazine- β -carboxylate, $\text{NHPh} \cdot \text{NH} \cdot \text{COOEt}$, are formed; the latter crystallises in long, white needles, melts at $80\text{--}81^\circ$, and is sparingly soluble in cold water, moderately soluble in cold, readily in boiling carbon bisulphide, and very soluble in cold alcohol and ether. This reaction tends to confirm the author's view of the constitution of ethyl carbethoxyacetoacetate, as no derivative of ethyl acetoacetate is known in which carboxethyl is detached from carbon by the action of phenylhydrazine. The pyrazolone is probably due to the secondary action of the hydrazine on ethyl

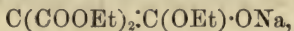
acetoacetate formed during the reaction, as on keeping an alcoholic solution of these two substances for some days, a very good yield of the pyrazolone was obtained (compare Knorr, *Annalen*, 238, 147).

No definite product was obtained from the action of alcoholic hydroxylamine on ethyl carbethoxyacetoacetate.

Ethyl acetomalonate, $\text{CHAc}(\text{COOEt})_2$, is formed, together with the corresponding diaceto-compound, when acetic chloride acts on ethyl sodiomalonate. It is an oily liquid boiling at 120° under 17 mm. pressure, readily soluble in aqueous alkalis, although with partial decomposition, and reprecipitated by acids. The *sodium derivative*, $\text{ONa}\cdot\text{CMe}\cdot\text{C}(\text{COOEt})_2$, prepared by adding the acetomalonate to an alcoholic solution of sodium ethoxide, crystallises in white, prismatic plates, is very soluble in water, fairly so in alcohol, but only sparingly in ether and concentrated aqueous potash. The presence of ketone carboxyl is proved by the formation of a *hydrazone*, $\text{N}_2\text{HPh}\cdot\text{CMe}\cdot\text{CH}(\text{COOEt})_2$, with phenylhydrazine acetate. This crystallises in white, prismatic plates, melts at $119\text{--}121^\circ$, and is insoluble in cold water, sparingly soluble in cold alcohol, and easily in hot alcohol.

Ethyl diacetomalonate, $\text{CAc}_2(\text{COOEt})_2$, or $\text{OAc}\cdot\text{CMe}\cdot\text{C}(\text{COOEt})_2$, formed as stated above, boils with slight decomposition at 156° , under 17 mm. pressure, and is neutral in its properties. When it is treated with phenylhydrazine (2 mols.) in ice-cold, ethereal solution, the acetyl is detached with the formation of β -acetylphenylhydrazine (m. p. $127\cdot5\text{--}128^\circ$).

Conrad and Gùthzeit's ethyl methanetricarboxylate (*loc. cit.*), as prepared by these authors' method, and also by the action of ethyl chlorocarbonate on an ethereal suspension of ethyl sodiomalonate, is not a neutral substance, as they state, but dissolves in aqueous alkalis, and forms a *sodium derivative*,



when treated with an alcoholic solution of sodium ethoxide. An attempt to methylate ethyl methanetricarboxylate by the Conrad-Limpach method yielded negative results.

The author is unable to confirm his previous statement (*Abstr.*, 1887, 716), as to the absorption of carbonic anhydride by ethyl sodiomalonate.

Ethyl acetylethylmalonate, $\text{CAcEt}(\text{COOEt})_2$, is prepared by adding acetic chloride to an ice-cold ethereal suspension of ethyl sodethylmalonate. It is a colourless, neutral oil, which boils with slight decomposition at $137\text{--}137\cdot5^\circ$ under 20 mm. pressure; is sparingly soluble in water, and is miscible with alcohol and ether. It is gradually decomposed by aqueous alkalis, but quickly by sodium ethoxide, ethyl carbonate and sodacetoacetate being formed. With phenylhydrazine acetate, it yields ethyl phenylhydrazine- β -carboxylate.

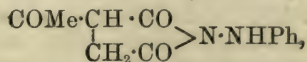
Ethyl acetomethylmalonate, prepared in a manner similar to that in which the ethyl compound is prepared, boils without decomposition at $131\text{--}131\cdot5^\circ$ (corr.), under 20 mm. pressure, is sparingly soluble in alcohol, and miscible with alcohol and ether. It is neutral towards aqueous alkalis, but is gradually decomposed by them. It is quickly

decomposed by sodium ethoxide into acetic and methyl- and ethyl-malonic acids.

Ethyl carbethoxymethylacetoacetate, $\text{COOEt} \cdot \text{O} \cdot \text{CMe} : \text{CMe} \cdot \text{COOEt}$, is prepared in a manner similar to that in which the corresponding ethyl compound is made. It is a colourless oil, which boils at 137° (corr.), under 20 mm. pressure. It is neutral towards aqueous alkalis, but is gradually decomposed by them, and quickly by sodium ethoxide, into ethyl carbonate and methyl acetoacetate. With phenylhydrazine, it behaves like the ethyl compound.

Ethyl propiomalonate forms a *sodium* derivative when treated with sodium ethoxide, and is soluble in aqueous alkalis, and reprecipitated by acids.

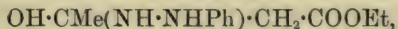
Ethyl sodacetosuccinate, prepared in the usual manner from ethyl acetosuccinate, purified by fractionation under 35 mm. pressure (b. p. $167-168^\circ$), yields *acetosuccinohydrazanil*,



when treated with phenylhydrazine in ethereal solution. This crystallises in large, white prisms, melts at $175-177^\circ$, and is soluble in the usual menstrua. It is dissolved by aqueous alkalis and precipitated unchanged by acetic acid. It forms a *sodium derivative*, $\text{C}_{12}\text{H}_{11}\text{NaO}_3\text{N}_2$, which is best prepared, however, by treating ethyl sodacetosuccinate (1 mol.) with free phenylhydrazine (1 mol.) in alcoholic solution, and crystallises in large prisms. It decomposes at 100° , and dissolves in water to a solution, from which it is partly precipitated by acetic acid; a certain amount of Knorr's ethyl acetosuccinate hydrazone (Abstr., 1884, 1380), is, however, formed at the same time. The difference in the behaviour of ethyl acetosuccinate and its sodium derivative towards phenylhydrazine thus points to a difference in constitution, probably of a merotropic character.

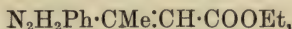
The phenylmethylpyrazolone mentioned above may be obtained in almost theoretical quantity by heating a mixture of ethyl acetoacetate and phenylhydrazine hydrochloride or other salt with a little strong hydrochloric or other mineral acid. Analogous results were obtained with the ethyl salts of methyl- and ethyl-acetoacetic and acetosuccinic acids. The hydrazone corresponding with phenylmethylpyrazolone is converted quantitatively into that substance, both by acids and by alkalis. Mineral acids do not prevent the formation of the hydrazones of fatty or aromatic aldehydes, as stated by Fischer, although they have a very marked retarding influence in the case of ketones.

Nef's contention that the formation of a hydrazo-derivative by the action of phenylhydrazine on ethyl acetoacetate renders the ketonic formula for the latter impossible, may be answered by the supposition that an intermediate additive compound

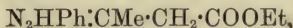


similar to Collie's compound, $\text{OH} \cdot \text{CMe}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{COOEt}$ (Abstr., 1885, 373), and to Kuckert's analogous compound with methylamine

and diethylamine (Abstr., 1885, 751), is first formed, and that this is transformed either into the hydrazo-derivative,



or under other conditions into the hydrazone,



with the elimination of water. This author considers this intermediate substance as typical, and would state generally that if a compound HX acts on a carbonyl compound with the elimination of water, an intermediate additive compound $\text{CX}\cdot\text{OH}$, is always formed. The elements of water eliminated from such a compound may be derived either from within the molecule, as in the above case, or from several molecules, in which case a condensation product is formed, or the hydroxyl may unite with the hydrogen of a foreign molecule.

The author then replies *seriatim* to many of Nef's statements and criticisms, and concludes by extending the positive-negative hypothesis to the explanation of the laws of addition to unsaturated compounds, and to the demonstration of the absence of necessity for the hypotheses of tautomerism and desmotropy. JN. W.

Relative Velocity of Lactone Formation in the case of Bibasic γ -Hydroxy-acids. By E. J. HJELT (*Ber.*, 25, 3173—3175).—The author has investigated the velocity of lactone formation in the case of the eight acids mentioned below. The method adopted has already been described (Abstr., 1891, 822). The solutions contained 0.00275 molecule (in grams), instead of 0.0055 molecule, and the temperature was 55°. The results are expressed by means of curves. The calculated times required for the conversion of 50 per cent. of the acids into the lactones were as follows:—

Itamalic acid	About 1900 minutes.
Phenylitamalic acid	475 "
Methylitamalic "	222 "
Isobutylitamalic "	110 "
Ethylitamalic "	100 "
Hexylitamalic "	82 "
Dimethylitamalic acid	49 "
Isopropylitamalic "	22 "

J. B. T.

Action of Sulphuric acid on β -Trimethylethylidenelactic acid. By T. SCHINDLER (*Monatsh.*, 13, 647—650).—The author finds that the compound formed by the action of sulphuric acid on β -trimethylethylidenelactic acid at 50°, and stated by Glücksmann to be trimethylacetaldehyde (compare Abstr., 1892, 38), is really methyl isopropyl ketone.

Trimethylethylidenelactic acid is oxidised by chromic acid mixture to trimethylacetic acid, which contains three methyl groups attached to one carbon atom. It therefore appears that sulphuric acid induces

a remarkable molecular rearrangement in the production of the ketone.

The aldehydic properties observed by Glücksmann were, no doubt, due to an admixture of some aldehyde with the ketone.

Attempts to obtain trimethylacetaldehyde by the action of hydrochloric acid on trimethylethylidenelactic acid were without success, the last-named acid remaining unchanged, both in the cold and at the boiling temperature.

G. T. M.

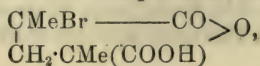
Mesitylic acid and Mesitonic acid. By H. WEIDEL and E. HOPPE (*Monatsh.*, **13**, 603—615; compare Anschütz and Gillet, *Abstr.*, 1888, 1272).—The authors show that mesitylic acid, $C_8H_{13}NO_3$, may be formed by the action of potassium cyanide, not only on the condensation product obtained from acetone and hydrochloric acid, but also on the condensation product of mesityl oxide and hydrochloric acid (compare Pinner, *Ber.*, **15**, 585).

When heated at 160—170° in sealed tubes, with concentrated hydrochloric acid, mesitylic acid loses carbonic oxide, carbonic anhydride, and ammonia, and is converted into mesitonic acid (dimethyllevulinic acid). With hydroxylamine hydrochloride, the latter gives a very characteristic isonitroso-compound, $C_7H_{13}NO_3$, which dissolves in all ordinary solvents, and melts at 94—95°; when heated by itself, it is converted into a lactone-like anhydride. This lactone is formed so readily that it must be supposed that the acid is itself capable of existing in the tautomeric form, $OH \cdot CMe \cdot CH \cdot CMe_2 \cdot COOH$.

G. T. M.

Stereoisomeric Derivatives of the Symmetrical Dimethylglutaric acids. By K. AUWERS and H. KAUFFMANN (*Ber.*, **25**, 3221—3247).—The authors have studied the reactions taking place during the bromination of the above acids. They find that the product obtained by the bromination of dimethylglutaric acid (m. p. 102—103°) depends on the varying conditions of the experiment and the mode of purification of the product, dibromodimethylglutaric acid, dibromodimethylglutaric anhydride (*Abstr.*, 1890, 1098), and two isomeric lactones ($C_7H_9BrO_4$) being formed, according to circumstances. The dibromo-acid is formed if the bromination is carried on at a low temperature and quickly, and the product of reaction, after treatment with ice, separated from the liquefied water as quickly as possible. When the bromination is carried on at a high temperature, the tendency is towards the formation of the anhydride; and if the product of reaction is allowed to remain in contact with the water, the less brominated lactones are produced.

Dibromodimethylglutaric acid, $C_7H_{10}Br_2O_4$, crystallises from benzene in prisms, melts with evolution of gas at 150°, and is soluble in alcohol, ether, water, and ethyl acetate, sparingly so in benzene. When an aqueous solution of this acid is allowed to remain at the ordinary temperature, hydrogen bromide is eliminated, and two isomeric lactones, $C_7H_9BrO_4$, of α -bromo- γ -hydroxydimethylglutaric acid are formed. One of these, of the probable formula

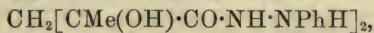


is sparingly soluble in cold water and ether, easily soluble in ethyl acetate, and nearly insoluble in benzene and light petroleum. It crystallises in needles, and melts at $196.5\text{--}197^\circ$, with blackening and evolution of hydrogen bromide. When the dibromo-acid is treated with *boiling* water, this lactonic acid forms by far the larger portion of the product, only small quantities of the more soluble acid being produced. It is tolerably stable towards water, but, by long-continued boiling with water, is gradually converted into the corresponding hydroxy-lactone $\text{C}_7\text{H}_{10}\text{O}_5$ (m. p. 188°) described by Zelinsky (Abstr., 1892, 436). The same change is readily caused by cold soda solu-

tion. The other *bromo-lactone*, $\text{CMe}(\text{COOH})-\text{CH}_2\text{CMeBrCO} > \text{O}$, is very much more soluble in water than its isomeride. It crystallises in plates or prisms, and melts at $111\text{--}113^\circ$ without decomposition. It is easily soluble in ether, ethyl acetate, and boiling benzene, almost insoluble in light petroleum. Like its isomeride, this lactone is stable towards water, but is converted by soda or by long-continued boiling with water into a dihydroxydimethylglutaric acid melting at 99° . The two bromo-lactones are, like the two dimethylglutaric acids, convertible into one another. When either lactone in benzene solution is heated at 160° , a mixture of the two is produced, but that of higher melting point is always present in the mixture in the larger proportion. When subjected to dry distillation, both acids decompose to a considerable extent, but the distillate always contains much of the lactone of high melting point, and little or none of that of low melting point. It is therefore clear that the lactone melting at 197° is the more stable at high temperatures.

Dibromodimethylglutaric anhydride, obtained by Auwers and Jackson by brominating dimethylglutaric acid (Abstr., 1890, 1098), was obtained by the author by the action of acetic chloride on the dibromo-acid. He finds the melting point to be $94\text{--}95^\circ$. In moist air, the anhydride is gradually reconverted into the dibromo-acid; with water, it forms the monobromo- and hydroxy-derivatives.

Dihydroxydimethylglutaric acid dihydrazide,



was formed by treating the hydroxy-lactone melting at 188° with phenylhydrazine. It crystallises in needles and melts at 176.5° .

A similar *dihydrazide*, crystallising, however, in needles melting at 186° , appears to be formed by the action of phenylhydrazine on the dihydroxy-acid.

The dimethylglutaric acid melting at 127° yielded, on bromination, mixtures of the monobromolactonic acids described above.

The authors also discuss fully the relationships of the isomeric derivatives of the two dimethylglutaric acids, and the probable constitutional explanation of the existence of such isomerides.

L. T. T.

Alkyl Tartrates. By P. FREUNDLER (*Compt. rend.*, 115, 509—512).—The author has prepared the methyl, ethyl, normal propyl, and isobutyl salts of diacetyltartaric, dipropionyltartaric, and dibutyryltartaric acids, as well as the normal butyl salts of diacetyltartaric

acid, by the action of the respective acid chlorides on the normal tartrates of the various alkyl radicles, and has determined their rotatory power. In the case of ethyl diacetyltartrate, the determination was made on the compound in a state of superfusion. All the salts are somewhat viscous, have very little odour, and can be distilled at the ordinary pressure without appreciable alteration of their rotatory power. This high stability of unsymmetrical compounds is noteworthy.

The specific rotatory powers, $[\alpha]_D$, are given in the following table:—

Alkyl base.	Acid.		
	Diacetyltartaric.	Dipropionyltartaric.	Dibutyryltartaric.
Methyl.....	(-14.29)*	-12.0	-13.0
Ethyl.....	+ 5.0	+ 0.3	- 1.0
Normal propyl..	+13.5	+ 7.9	+ 5.4
Normal butyl ..	+17.8	—	—
Primary isobutyl	+11.3	+ 9.2	+ 7.1

* Pictet's value.

These results verify the law of the change of sign of the rotatory power. Each compound contains two equal masses ($\text{Me}\cdot\text{CO}\cdot\text{O}$ and COOMe ; $\text{Et}\cdot\text{CO}\cdot\text{O}$ and COOEt ; and $\text{Pr}\cdot\text{CO}\cdot\text{O}$ and COOPr), and if these two masses were concentrated exactly on the summits of the tetrahedron representing the asymmetrical carbon, the three compounds would remain inactive. The fact that they are optically active confirms Guye's view that although the mass constituting the principal factor allows of the prediction of the sign of optical activity, it is necessary to take into account the arrangement of the atoms.

C. H. B.

Action of Phosphorus Oxychloride on Aromatic Silicates.

By H. N. STOKES (*Amer. Chem. J.*, **14**, 545—547).—Phenyl orthosilicate (1 mol.), unlike the aliphatic silicates, does not yield chlorobenzene and silicopyrophosphoryl chloride when heated with phosphorus oxychloride (2 mols.) for 16 hours at 240° , but silicon tetrachloride, phenylphosphoric chloride, $\text{POCl}_2\cdot\text{OPh}$, and diphenylphosphoric chloride, $\text{POCl}(\text{OPh})_2$.

JN. W.

Preparation of Orthonitrobenzyl Alcohol. By H. G. SÖDERBAUM and O. WIDMAN (*Ber.*, **25**, 3290—3291; compare Paal and Bodewig, this vol., i, 20).—Orthonitrobenzyl alcohol is readily obtained by boiling orthonitrobenzyl chloride (10 grams) with anhydrous potassium carbonate (8 grams) and water (150 c.c.) for four hours in a reflux apparatus; the alcohol separates on cooling, and is purified by recrystallisation from benzene; the yield is 50 per cent. of the chloride employed.

J. B. T.

Benzyl Silicate. By H. N. STOKES (*Amer. Chem. J.*, **14**, 547).—Benzyl alcohol reacts violently with silicon tetrachloride, like an aliphatic alcohol, and not gently, like a phenol. As much as one-fourth of the alcohol is converted into benzyl chloride, and a corresponding amount of the silicon chloride is in consequence converted

into polysilicates. The benzyl silicate which is formed may be separated by distillation, but decomposes on redistillation.

JN. W.

Behaviour of Thiocarbonates towards Phenols. By R. PRIBRAM and C. GLÜCKSMANN (*Monatsh.*, **13**, 623—634).—*Resorcinol-carbothionylic acid* is obtained by heating together at 100° resorcinol and potassium thiocarbonate. It sinters at 150°, melts at 150—155°, gives a red coloration with excess of potash, and, when heated with an excess of alkali hydroxide, yields metadihydroxybenzoic acid, $[\text{COOH}:(\text{OH})_2 = 1:2:4]$, as chief product. The bye-product probably consists of 2:6-dihydroxybenzoic acid, and there is no indication that any dihydroxyphthalic acid is formed. G. T. M.

Pyrogallol Antimonites. By H. CAUSSE and C. BAYARD (*Compt. rend.*, **115**, 507—509).—100 grams of antimony trichloride is dissolved in 250 c.c. of a solution of sodium chloride saturated at the ordinary temperature, and the filtered liquid is poured in successive small quantities into a solution of 50 grams of pyrogallol in 250 c.c. of the salt solution. A white, flocculent precipitate separates, and, as soon as this ceases to form, no more antimony chloride is added, and the precipitate is left in contact with the liquid for some hours. It gradually becomes much denser, and changes into a mass of small crystals, which is pressed between filter-paper, dried, washed until free from sodium chloride, and again dried at the ordinary temperature. The product is *pyrogallol hydrogen antimonite*, $\text{OH}\cdot\text{C}_6\text{H}_3\cdot\text{O}_2\text{SbOH}$. It has the same properties as the corresponding catechol derivative (Abstr., 1892, 1078), and consists of microscopic crystals, insoluble in water, alcohol, benzene, and chloroform, but soluble in nitric, sulphuric, and hydrochloric acids, by the latter of which it is completely decomposed.

The *normal antimonite*, $\text{C}_6\text{H}_3\cdot\text{SbO}_3$, is obtained in a similar manner from hot solutions. The pyrogallol solution is heated on a water-bath, and the whole quantity of antimony chloride solution is added. In its general properties, the normal antimonite very closely resembles the hydrogen salt.

Acetic anhydride acts on the normal or hydrogen salt at 100° with production of pyrogallol triacetate. Acetic chloride acts with almost explosive violence, and likewise yields pyrogallol triacetate.

It would seem from these results that the third hydroxyl group in pyrogallol occupies the meta-position, and not the para-position, as is generally assumed.

C. H. B.

Metamidodialkylorthotoluidines and their Conversion into Methylene-blue Dyes. By A. BERNTHSEN (*Ber.*, **25**, 3128—3139).—According to Weinberg (Abstr., 1892, 1078), paramidodialkylorthotoluidines do not yield thiosulphonic acids, neither could a thionine dye be obtained. This is not in accordance with the author's views of the formation of the methylene-blue compounds (Abstr., 1889, 775). The author now finds that metamidodimethylorthotoluidine $[\text{Me}:\text{NMe}_2:\text{NH}_2 = 1:2:5]$ and orthamidodimethylmetatoluidine $[\text{Me}:\text{NMe}_2:\text{NH}_2 = 1:3:6]$ yield thiosulphonic acids and methyl-

ene-blue compounds. The amidodimethylorthotoluidine was prepared by methylating nitro-orthotoluidine, purifying the dimethyl compound, and then reducing it.

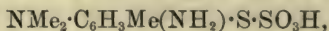
Metanitroorthotoluidine (60 grams) is heated with methyl iodide (150 grams), sodium hydroxide (35 grams), and methyl alcohol (180 c.c.) in an autoclave for 8—10 hours at the boiling point of a saturated solution of salt. The mixture of mono- and di-methyl compounds is separated either by boiling with acetic anhydride and then distilling the dimethylnitrotoluidine with steam; or by treating the mixture with dilute sulphuric acid (200—250 c.c., sp. gr. = 1.15), when the dimethyl compound only is dissolved.

Metanitromethylorthotoluidine [$\text{Me} : \text{NHMe} : \text{NO}_2 = 1 : 2 : 5$] is less soluble in alcohol than the dimethyl compound, crystallises in beautiful yellow tablets, and melts at 137° . The *nitrosamine* is obtained as a colourless oil by adding a solution of sodium nitrite to a solution of nitromethyltoluidine in hydrochloric acid. It solidifies after a time and melts at 65° . The *acetyl compound* crystallises from dilute alcohol in pale yellow, rhombohedral crystals, melts at 97° , and is very easily soluble in alcohol.

Metanitrodimethylorthotoluidine [$\text{Me} : \text{NMe}_2 : \text{NO}_2 = 1 : 2 : 5$] crystallises in small tablets or needles, melts at 47.5° , is very easily soluble in organic solvents, sparingly so in water, and dissolves in dilute hydrochloric and sulphuric acids; from the latter solvents it is precipitated by the addition of water.

Metamidodimethylorthotoluidine is obtained by reduction of the preceding compound with hydrochloric acid and zinc-dust. It boils at $253\text{--}254^\circ$, is a colourless oil, which soon turns brown on exposure to air; it solidifies when strongly cooled, and melts at 47° . The *sulphate* crystallises in beautiful white needles, and is easily soluble in water, sparingly so in alcohol. A dilute neutral solution of the salt gives with ferric chloride an intense bluish-red coloration, which turns violet on the addition of hydrochloric acid, and, on heating, the odour of quinone is observed. With potassium dichromate, a similar purplish-red is produced. With an alkaline solution of α -naphthol and potassium ferricyanide, it gives the intense blue of the indophenol reaction. With dichromate and dimethylaniline hydrochloride, a deep green indamine is produced. The pure base does not yield a thionine dye when treated with hydrogen sulphide and ferric chloride.

Dimethylparatolylenediamine hydrogen thiosulphate,



is obtained from dimethylparatolylenediamine in almost theoretical quantities by the method formerly described (*Annalen*, **251**, 50). It crystallises in small, thick prisms, melts at about 240° with decomposition, and is very sparingly soluble in cold water, more easily in hot water and hydrochloric acid. In aqueous solution, it gives colour reactions similar to those of amidodimethylaniline hydrogen thiosulphate. When warmed with soda, it yields the *bisulphide* of amidodimethyl-orthotoluidine; when reduced with zinc-dust and hydrochloric acid, the *mercaptan*, $\text{NMe}_2 \cdot \text{C}_6\text{H}_2\text{Me}(\text{NH}_2) \cdot \text{SH}$, is obtained. Both these compounds give an easily soluble indamine sulphide with dimethylaniline.

Tetramethylhomoindamine thiosulphate, $C_{17}H_{21}N_3S_2O_3$, is obtained from the above amidodimethylorthotoluidine by converting it into the acid thiosulphate, and, after a few minutes, adding an aqueous solution of dimethylaniline hydrochloride and the calculated quantity of chromate. The product is obtained in slender, green needles, and is purified by washing with dilute acetic acid. It crystallises with 1 mol. H_2O , which it loses at $90-95^\circ$.

Homomethylene-blue, $C_{17}H_{20}N_3S$, is obtained from the preceding compound in the manner formerly described for methylene-blue, which it closely resembles. The *hydriodide* crystallises with 1 mol. H_2O in small needles, and is very sparingly soluble in water.

The mono- and di-ethyl derivatives of metanitro-orthotoluidine are obtained in a similar way to the methyl derivatives. The mixed product is purified by crystallising the free bases from a small quantity of alcohol, in which the monethyl derivative is less soluble. The diethyl compound is then purified in the same way as described for the dimethyl compound by means of acetic anhydride.

Nitroethylorthotoluidine crystallises from alcohol in large, dark yellow plates, and melts at 98° . The *acetyl compound* crystallises from dilute alcohol in colourless tablets or prisms, and melts at $96-97^\circ$.

Metanitrodiethylorthotoluidine is obtained as a yellow oil by distillation with steam and is sparingly soluble in water, easily so in dilute hydrochloric or sulphuric acid.

Metamidodiethylorthotoluidine is a colourless oil which quickly darkens on exposure to air, and boils at $266-267^\circ$. The *sulphate*, $C_{11}H_{18}N_2H_2SO_4$, crystallises in large, colourless tablets. The dilute aqueous solution of the salt gradually develops a purple-red coloration when mixed with ferric chloride, and with dichromate, a red coloration. With α -naphthol and potassium ferricyanide, it gives a violet-red, with dimethylaniline hydrochloride and dichromate, a dirty, reddish-brown precipitate.

Amidodiethylorthotoluidine hydrogen thiosulphate is not obtained so readily as the dimethyl compound. It crystallises in small, colourless prisms, and melts at $210-215^\circ$. With soda, it yields a bisulphide; with zinc and hydrochloric acid, a mercaptan; both these compounds give indamines. It gives a blue dye, having the characteristic properties of the thionine dyes.

E. C. R.

Metamidodialkylorthotoluidines and their Conversion into Methylene-blue Dyes. By A. BERNTHSEN (*Ber.*, 25, 3366—3368; compare preceding abstract).—The author has previously shown that the amidodiethylorthotoluidine, $C_6H_3Me(NEt_2) \cdot NH_2$, [$1 : 2 : 5$], prepared by ethylating the nitrotoluidine [$Me : NH_2 : NO_2 = 1 : 2 : 5$] and reducing the resulting product, when oxidised with chromate, in the presence of a thiosulphate, yields amidodiethylorthotoluidine hydrogen thiosulphate, $NEt_2 \cdot C_6H_3Me(NH_2) \cdot S \cdot SO_3H$. Weinberg (*Abstr.*, 1892, 1078) was unable to effect this conversion, but he prepared his base from metamidoethylorthotoluidine by acetylating, ethylating, and eliminating the acetyl group. It is now shown that this method gives an impure product, but the pure base

can be isolated from it, and then yields the thiosulphate mentioned above. C. F. B.

Conversion of Tanacetoxime into 1 : 3 : 4-Cymidine. By F. W. SEMMLER (*Ber.*, 25, 3352—3354).—If an alcoholic solution of tanacetoxime (this vol., i, 107) is boiled and a mixture of dilute sulphuric acid and alcohol gradually added, a portion of the oxime is converted into the hitherto unknown *cymidine*, $C_6H_3Pr^{\beta}Me \cdot NH_2$ [$Pr^{\beta} : NH_2 : Me = 1 : 3 : 4$], which was identified by converting it, by the diazo-reaction, into 1 : 3 : 4-carvacrol. It is a basic substance which boils at 118—121° under 13 mm. pressure, and has a sp. gr. of 0.9442 at 20°, and refraction $[n]_D = 1.5387$. Its odour resembles that of aniline, and at the same time that of thymol; it forms a sparingly soluble sulphate, its hydrochloride colours a deal splinter yellow, and it gives a red coloration with bleaching powder. When its platinumchloride is heated with excess of platinic chloride, the solution turns green, then violet-blue, and finally red, and yields a deep blue, or a red, colouring matter when extracted with ether. C. F. B.

Condensation Products of Amidophenols and Amidophenyl Ethers with Aldehydes and Ketones. By C. PHILIPP (*Ber.*, 25, 3247—3249).—The author obtained benzylideneparamidophenol by the action of benzaldehyde on a hot aqueous solution of paramidophenol hydrochloride and sodium acetate, and also by the admixture of alcoholic solutions of the phenol and aldehyde. He finds the melting points to be 181°; Haegele (*Abstr.*, 1892, 1451) gave it as 163°. It combines with mineral and organic acids to form very stable additive products, crystallising in yellow needles. The etheric derivatives are obtained by direct substitution or by condensation of phenol ethers.

Benzylideneparamidomethoxybenzene, $CHPh \cdot N \cdot C_6H_4 \cdot OMe$, forms colourless scales melting at 62°. The *ethoxy*-derivative forms colourless scales melting at 76°. L. T. T.

Acidoxyl Derivatives of Diphenylethylenediamine and Ditolythylenediamine. By C. A. BISCHOFF and A. HAUSDÖRFER (*Ber.*, 25, 3253—3262).—The following compounds, containing nitrogen atoms combined with three different radicles, described in this and the next abstract, and on p. 98, were prepared in order to determine if they exist in stereometric modifications. In no case was a stereometric isomeride obtained.

Dimonochloracetyldiphenylethylenediamine, $C_2H_4(NPh \cdot CO \cdot CH_2Cl)_2$, is obtained, together with diphenylethylenediamine hydrochloride, by the action of chloracetic chloride on diphenylethylenediamine dissolved in ether. It crystallises in colourless, oblique prisms, and melts at 153—154°.

Dimonobromacetyldiphenylethylenediamine, obtained in a similar way to the preceding compound, crystallises in large prisms, and melts at 136°.

Dimonobromopropionyl diphenylethylenediamine is obtained together with diphenylethylenediamine hydrobromide by the action of bromo-

propionic bromide on diphenylethylenediamine dissolved in benzene. It is separated from the above hydrobromide by extracting the product with benzene, in which the latter is insoluble. It crystallises in small, dull tablets, and melts at 184° .

Di- α -monobromonormalbutyryldiphenylethylenediamine crystallises in transparent tablets, and melts at 98° .

Di- α -monobromisobutyryldiphenylethylenediamine crystallises in white, uncharacteristic crystals, and melts at 143° .

Diacetyldiorthotolylethylenediamine, $C_2H_4(NAc \cdot C_7H_7)_2$, is obtained in theoretical quantity by adding acetic anhydride to orthoditolylethylenediamine. It crystallises in colourless prisms, and melts at $152-153^{\circ}$.

Dimonobromacetyldiorthotolylethylenediamine crystallises in colourless needles, and melts at 205° .

Dimonobromopropionyldiorthotolylethylenediamine is obtained as a white, viscous mass which, on extraction with benzene, yields a product melting at $139-180^{\circ}$. By crystallisation from ether, it is obtained in oblique prisms, melting at 181° . To determine if a lower-melting isomeride is present in the crude product, a quantitative experiment was made. The theoretical yield of the acidoxyl compound was obtained melting between 176° and 181° , together with diorthotolylethylenediamine hydrobromide in molecular proportion.

Di- α -bromonormalbutyryldiorthotolylethylenediamine crystallises with 1 mol. of benzene, and melts at 190° .

Di- α -bromisobutyryldiorthotolylethylenediamine is obtained, together with monobromisobutyryldiorthotolylethylenediamine melting at $135-137^{\circ}$, in a similar way to the preceding compounds. It crystallises in colourless, rhombohedral tablets, and melts at $172-173^{\circ}$.

Diacetyldiparatolylethylenediamine crystallises in colourless, rhombohedral prisms and melts at $137-139^{\circ}$.

Dimonobromacetyldiparatolylethylenediamine crystallises in colourless, transparent parallelopipeds, and melts at 196° .

Di- α -bromopropionyldiparatolylethylenediamine melts at 182° , and otherwise resembles the preceding compound.

Di- α -bromonormalbutyryldiparatolylethylenediamine melts at 125° , has similar properties to the preceding compound, but is more easily soluble in ether and light petroleum.

Di- α -monobromisobutyryldiparatolylethylenediamine crystallises in colourless, long, six-sided prisms, melts at 175° , and has the same solubility as the preceding compound, but is more sparingly soluble in ether and light petroleum.

The solubilities of these compounds in the ordinary solvents are described at length. E. C. R.

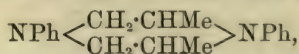
Derivatives of Propylenediamine and Pseudobutylenediamine. By C. TRAPESONZIANZ (*Ber.*, 25, 3271—3282).—*Diphenylpropylenediamine*, $NHPh \cdot CHMe \cdot CH_2 \cdot NHPh$, is obtained by the action of propylene bromide on aniline. It is a very viscid, colourless oil, and boils at 265° under 60 mm. pressure. The *hydrochloride* crystallises in spherical aggregates, turns red on exposure to air, and melts at

100° with evolution of gas. The *platinochloride* is obtained as a yellow precipitate. The *diacetyl* compound forms irregular crystals, and melts at 146—147°. The *dibenzoyl* derivative crystallises in long, white tablets, and melts at 136—137°.

Propylenediphenylcarbamide, $\text{CO} \begin{smallmatrix} \text{NPh} \cdot \text{CHMe} \\ | \\ \text{NPh} \cdot \text{CH}_2 \end{smallmatrix}$, is obtained by adding carbonyl chloride to diphenylpropylenediamine both dissolved in benzene. It melts at 121—122°, is easily soluble in hot alcohol, benzene, chloroform, and carbon bisulphide, and insoluble in water; it dissolves in concentrated sulphuric acid, from which it is precipitated by adding water, and is not attacked by boiling aqueous potash.

Methyldiphenylpiperazine, $\text{NPh} \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{NPh}$, is obtained by heating diphenylpropylenediamine with ethylene bromide and anhydrous soda at 150°. It crystallises in small, white prisms, melts at 100°, and is easily soluble in benzene, chloroform, carbon bisulphide, hot alcohol, and ether, less so in light petroleum, insoluble in water, and dissolves in warm concentrated sulphuric acid. It cannot be prepared by heating propylene bromide with diphenylethylenediamine and soda at 160°. The influence of the methyl group in propylene bromide is also seen by the fact that in the preparation of diphenylethylenediamine, larger or smaller quantities of the tertiary base (diphenylpiperazine) are always formed, whereas in the preparation of the corresponding propylene base, only the secondary base is formed. Also the bases obtained by the action of aniline and toluidine on propylene bromide are oily liquids, whereas those obtained from ethylene are all solid compounds. The author explains this influence of the methyl group by Bischoff's hypothesis (Abstr., 1891, 892).

Diphenyldimethylpiperazine, $\text{NPh} \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CHMe} \end{smallmatrix} \text{NPh}$ or



is obtained by heating diphenylpropylenediamine with propylene bromide at 140—150° for five hours. A viscid colourless oil is obtained which boils at 250—270° under 50 mm. pressure, and is contaminated with diphenylpropylenediamine, which the author was unable to eliminate.

Diorthotolylpropylenediamine, $\text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_7\text{H}_7$, is obtained by heating orthotoluidine with propylene bromide in a reflux apparatus at 150—160°. It boils at 250—265° under a pressure of 70 mm., and at 280° under 120 mm. The *diacetyl* derivative crystallises in small, oblong tablets, and melts at 101—102°.

Propylenediorthotolylcarbamide, $\text{CO} \begin{smallmatrix} \text{N}(\text{C}_7\text{H}_7) \cdot \text{CHMe} \\ | \\ \text{N}(\text{C}_7\text{H}_7) \cdot \text{CH}_2 \end{smallmatrix}$, obtained by the action of carbonyl chloride on the above diamine, crystallises from dilute alcohol in small, irregular prisms, melts at 93°, and is soluble in the ordinary solvents with the exception of light petroleum.

Diparatolylpropylenediamine, obtained in a similar way to the ortho-compound, is a pale-yellow oil, and boils at 276—278° under 48 mm. pressure. The *diacetyl* compound crystallises from alcohol and ether in small, white prisms, and melts at 113·5—114°. The *dibenzoyl* compound melts at 151—152°.

Propylenediparatolylcarbamide crystallises in small, colourless prisms, melts at 129·9°, and is easily soluble in benzene, chloroform, alcohol, and carbon bisulphide, less so in ether, and insoluble in light petroleum.

Diparatolylmethylpiperazine is obtained by heating diparatolylpropylenediamine with ethylene bromide and anhydrous soda for one hour at 150°. It crystallises from alcohol in small, white needles, melts at 105°, and is easily soluble in most solvents, less so in light petroleum.

Di-α-naphthylpropylenediamine is obtained by heating a mixture of α-naphthylamine, propylene bromide, and dry sodium carbonate at 165° for 1—1½ hours. It crystallises in small, white aggregates, and melts at 218—220°.

Di-β-naphthylpropylenediamine is obtained, together with dinaphthylamine, by heating a mixture of β-naphthylamine and propylene bromide at 170—180°. The formation of dinaphthylamine may be prevented by adding dry soda to the mixture. The *hydrochloride* crystallises in small aggregates, and melts at 190—191°.

Propylenedi-β-naphthylcarbamide crystallises in slender needles, melts at 157°, and is easily soluble in benzene, chloroform, hot acetone, and acetic acid.

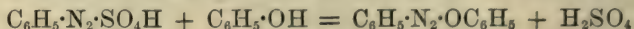
Diphenyldimethylethylenediamine, $\text{NPh}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{NPh}$, is obtained by heating a mixture of aniline and pseudobutylene bromide at 160° for four hours. It is a pale-yellow oil, and boils at 225—228° under 41 mm. pressure. The *hydrochloride*, $\text{C}_{16}\text{H}_{22}\text{N}_2\text{Cl}_2$, crystallises in short needles, melts at 205°, and decomposes at 230°. The *diacetyl derivative* crystallises in small, prismatic tablets, and melts at 195—196°. The *dibenzoyl derivative* is precipitated from chloroform by absolute ether in small, crystalline aggregates, and melts at 243—244°.

Dimethylethylenediphenylcarbamide, $\text{CO} < \begin{array}{c} \text{NPh}\cdot\text{CHMe} \\ | \\ \text{NPh}\cdot\text{CHMe} \end{array}$, crystallises in white prisms, melts at 139—141°, and is easily soluble in most solvents, sparingly so in petroleum, and insoluble in water.

E. C. R.

Decomposition of Diazo-compounds. By J. HAUSER and P. T. MULLER (*Compt. rend.*, 114, 1438—1441).—The decomposition of diazo-compounds by water, as the authors have already shown (*Abstr.*, 1892, 768), does not in all cases follow the ordinary laws of mass action. To the substances formerly mentioned as abnormal in their behaviour must now be added diazobenzene sulphate, in the decomposition of which a retardation occurs similar to that previously noted in the other instances. The authors show that the explanation which they have already given of this retardation is correct, and that

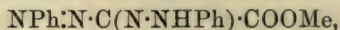
it is due to the influence of the phenol liberated during the reaction. As Hirsch has shown, phenol does react with diazobenzene salts (Abstr., 1891, 437), and an action in the sense of the equation



may, perhaps, take place. Other derivatives, however, exercise a retarding influence on the above reaction, whereas open-chain compounds such as alcohol, oxalic acid, and sugar are without effect. The influence must, therefore, in some manner depend on the benzene nucleus. H. C.

Action of Diazobenzene on Malonic acid. By H. v. PECHMANN (*Ber.*, 25, 3175—3190).—It is already known that the compound obtained by the action of malonic acid on diazobenzene is identical with that formed from mesoxalic acid and phenylhydrazine; on treating ethyl mesoxalate hydrazone with acetic anhydride, carbonic anhydride is evolved and *ethyl glyoxylate acetylhydrazone*, $\text{NPhAc}\cdot\text{N}\cdot\text{CH}\cdot\text{COOEt}$, is formed; it crystallises from alcohol, melts at 95° , and, on hydrolysis, yields glyoxylic acid hydrazone; the correctness of the hydrazone formula for the original compound is thus finally proved.

By the action of ethyl mesoxalate hydrazone on diazobenzene chloride in molecular proportion at low temperatures, a compound is obtained which has the formula $\text{NPh}\cdot\text{N}\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{COOEt}$, and crystallises from alcohol in lustrous, brownish-yellow plates; these when allowed to remain in contact with the mother liquor change into red prisms with a blue fluorescence; both forms melt at 117.5° when quickly heated; the compound is also formed from ethyl sodiummalonate and anhydrous diazobenzene chloride in alcoholic solution, and from diazobenzene and ethyl benzeneazoacetate, or directly from ethyl acetoacetate (compare Bamberger, Abstr., 1892, 162). The author suggests the name *ethyl formazylcarboxylate* for the compound, the group $\text{NPh}\cdot\text{N}\cdot\text{C}\cdot\text{N}\cdot\text{NHPh}$ being termed *formazyl*. The yield is almost quantitative. The *acetyl derivative* is formed by heating the substance with zinc chloride and acetic anhydride; it crystallises in yellow needles. *Methyl formazylcarboxylate*,



is prepared by dissolving ethyl malonate (1 mol.) in sodium methoxide (1 mol.) solution, and adding it gradually to diazobenzene chloride (1 mol.) in methyl alcoholic solution, the temperature not being allowed to exceed 0° ; it crystallises from methyl alcohol in red needles melting at $134\text{--}135^\circ$, and, on hydrolysis, yields the same acid as the ethyl salt; molecular weight determinations agree with the above formula. The yield is equal to about half the ethyl malonate employed. *Methyl mesoxalate hydrazone*, which crystallises in yellow needles melting at 129° , also yields methyl formazylcarboxylate on treatment with diazobenzene chloride.

Formazylcarboxylic acid, $\text{NPh}\cdot\text{N}\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{COOH}$, is prepared by dissolving either the ethyl or methyl salt in 10 parts of alcohol,

and boiling the solution for five minutes with 5 parts of soda (12 per cent.); the precipitated acid is purified by solution in potash and crystallisation from dilute alcohol; it is deposited in small, red needles, melts at $162\text{--}163^\circ$ with decomposition, and is readily soluble in benzene or chloroform, but sparingly so in alcohol and ether. The salts are sparingly soluble and red or brown in colour; the *potassium salt* crystallises in small, lustrous plates; the *silver salt* is violet coloured, and, on treatment with methyl iodide or ethyl iodide, yields the methyl and ethyl salts previously described.

Formazyl hydride, $\text{NPh}\cdot\text{N}\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$, may be obtained in three ways: (1) By heating formazylcarboxylic acid, carbonic anhydride being evolved. (2) By heating phenylhydrazine (3 parts) with ethyl formate (1 part) and alcohol (8 parts) for 24 hours in a reflux apparatus; this is the best method of preparing formylphenylhydrazine (m. p. 145°); the yield of hydrogen formazyl is 40 per cent. of the ethyl formate employed. (3) Malonic acid (26 grams), and sodium acetate (50 grams) are dissolved in ice-cold water (400 grams) and quickly mixed with half the theoretical quantity (1 mol.) of diazobenzene chloride solution, prepared from aniline (23 grams), hydrochloric acid, sp. gr. 1.19 (57 grams), sodium nitrite (18 grams), and sodium acetate (50 grams); the mixture is allowed to remain for 12—15 hours at 0° , the deposited product is separated, washed, dried, and dissolved in methyl alcohol, the solution, after being freed from resinous matter by the cautious addition of water, is diluted, and the product purified by repeated crystallisation from methyl alcohol. The yield is equal to the malonic acid employed. Formazyl hydride is deposited in small, red needles which exhibit a violet lustre, and melt at $116\text{--}119^\circ$ with previous softening at 100° . The *acetyl derivative* is prepared by heating formazyl hydride with 4 parts of acetic anhydride, to which zinc chloride has been added, but it may be obtained more readily from the carboxylic acid; it crystallises from alcohol or acetone in orange-yellow needles melting at $188\text{--}189^\circ$, and gives a blue coloration with sulphuric acid.

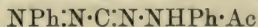
By the action of zinc dust (0.5 part) and acetic anhydride (3—4 parts) on formazyl hydride, or on its acetyl derivative, the *diacetyl derivative* of a reduction compound, $\text{N}_2\text{HPhAc}\cdot\text{CH}\cdot\text{N}\cdot\text{NAcPh}$, is obtained; it crystallises from alcohol, in which it is sparingly soluble, in small, rhombic plates, melts at 197° , and gives a red coloration with alkalis, and a pale-yellow with ferric chloride. In the preparation of the preceding compound, a *monacetyl derivative*, $\text{N}_2\text{HPhAc}\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$, is also formed; this crystallises in needles, melts at $163\text{--}164^\circ$, gives no coloration with ferric chloride, and is readily converted into the above diacetyl derivative.

Formazylazobenzene, $\text{NHPh}\cdot\text{N}\cdot\text{C}(\text{N}\cdot\text{NPh})_2$, is formed by the action of diazobenzene chloride on formazylcarboxylic acid or mesoxalic acid hydrazene in alkaline solution; it is, however, most readily prepared from diazobenzene chloride (3 mols.) and malonic acid (1 mol.) in presence of sodium acetate. The product is purified by repeated crystallisation from alcohol, and is deposited in dark-red, bronze, lustrous plates melting at $162\text{--}163^\circ$; it is readily soluble in chloroform, acetone, or benzene, and gives a blue coloration with sulphuric

acid, changing to red on the addition of water ; with reducing agents, a colourless compound is formed.

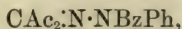
J. B. T.

Mixed Azo-compounds. By H. v. PECHMANN (*Ber.* 25, 3190—3200).—The compound prepared by Pechmann and Jenisch (compare *Abstr.*, 1892, 161) from acetonedicarboxylic acid and diazobenzene proves to be *mesoxalic dihydrazone*, $\text{CO}(\text{CH}:\text{N}\cdot\text{NHPH})_2$, not disbenzeneazoacetone, $\text{CO}(\text{CH}_2:\text{N}:\text{NPh})_2$, since, on heating with acetic anhydride and zinc chloride, it yields a *diacetyl derivative*, $\text{CO}(\text{CH}:\text{N}\cdot\text{NAcPh})_2$, which crystallises in yellow needles, melts at $167\text{--}168^\circ$, and yields acetanilide. The compound, believed by Bamberger to be the symmetrical hydrazone of mesoxalic aldehyde (*Abstr.*, 1892, 162), proves to be *formazyl methyl ketone*,



(compare next abstract). It would appear from the above, as well as from the researches of Japp and Klingemann, that all compounds formed from diazobenzene and 1 : 3-diketo-derivatives must be hydrazines. Beyer and Claisen showed that benzeneazoacetylacetone (from acetylacetone and diazobenzene) has the formula $\text{CHAc}_2\cdot\text{N}_2\text{Ph}$, since it yields a hydrazone which is readily converted into a pyrazole derivative. By the introduction of an acid radicle into the molecule of benzeneazoacetylacetone and subsequent decomposition of the product, acid anilides are obtained, showing that one of the hydrogen atoms of the original compound must be linked to nitrogen ; the compound is probably tautomeric, since, in some respects, it behaves as an azo-derivative ; but in the free state it appears to be represented by the hydrazine formula, as it reacts with sulphuric acid and potassium dichromate.

The *benzoyl derivative* of "benzeneazoacetylacetone,"



is prepared from the sodium salt by benzoic chloride ; it crystallises from alcohol in lustrous, rhombic plates, melts at $160\text{--}161^\circ$, and gives a brown coloration with sulphuric acid and potassium dichromate. On treatment with stannous chloride and hydrochloric acid, benzanilide is formed.

The *acetyl derivative*, $\text{CAc}_2\cdot\text{N}\cdot\text{NPhAc}$, is prepared from the hydrazone by the action of acetic anhydride and zinc chloride ; it crystallises from dilute alcohol in lustrous, rectangular plates, melts at $145\text{--}146^\circ$, and yields acetanilide.

The author then proceeds to show at length, by means of formulæ, how hydrazine derivatives may be formed when diazobenzene acts on various substances ; he suggests that the process is analogous to the aldol condensation, and, excluding a few cases where experimental evidence is wanting, concludes that the compounds of diazobenzene with aliphatic derivatives are hydrazines.

J. B. T.

Action of Diazobenzene on Ethyl Acetoacetate. By E. BAMBERGER and E. WHEELWRIGHT (*Ber.*, 25, 3201—3213 ; compare v. Pechmann, preceding abstracts).—Ethyl formazylcarboxylate,

$\text{NPh}\cdot\text{NC}\cdot\text{N}\cdot\text{NHPh}\cdot\text{COOEt}$, has been prepared, independently of the authors, by the action of ethyl acetoacetate (1 mol.) on diazobenzene (2 mols.); the *silver salt*, $\text{NPh}\cdot\text{N}\cdot\text{C}(\text{N}\cdot\text{NAgPh})\cdot\text{COOEt}$, is brownish-red. *Sodium formazylcarboxylate* crystallises in small, lustrous, dark red needles, and melts at $200\text{--}201^\circ$ with evolution of gas; the *ammonium salt* is also crystalline, and readily soluble; the *barium*, *calcium*, *zinc*, *lead*, and *copper salts* have been prepared; they are all dark red, and sparingly soluble.

Formazylhydrazide has already been described (*loc. cit.*); it may also be obtained by heating the acid for a considerable time with alcoholic potash.

Formazylazobenzene (phenylazoformazyl), $\text{C}(\text{NPh}\cdot\text{N})_2\cdot\text{N}\cdot\text{NHPh}$, crystallises in needles and also in dark red, lustrous plates; its formation from diazobenzene and pyruvaldehydephenylhydrazone has already been described (Abstr., 1892, 162); it is, however, obtained by the action of diazobenzene on acetone, acetaldehyde, and pyruvic acid, all of which contain a methyl group linked to the carbonyl group. By the action of mineral acids on the ethereal salts of formazylcarboxylic acid, aniline and phenazine are formed, together with a third compound, which crystallises in orange-red, lustrous needles, and melts at $74\text{--}75^\circ$; it has the formula $\text{C}_7\text{H}_5\text{N}_3$, and is probably identical with α -phenotriazine.

The authors suggest that in the formazyl group the position of different radicles should be indicated by the prefix *a* or *b*, according to whether the radicle be linked to the "azo-" or to the hydrazine group; they consider that the action of diazobenzene on aldehydes or ketones (in strongly alkaline solution) proceeds according to one or more of the following three typical equations:—

1. $\text{R}_1\cdot\text{CO}\cdot\text{CH}_2\cdot\text{R} + \text{N}_2\text{Ph}\cdot\text{OH} = \text{R}_1\cdot\text{CO}\cdot\text{CR}\cdot\text{N}\cdot\text{NHPh} + \text{H}_2\text{O}.$
2. $\text{R}\cdot\text{CO}\cdot\text{CH}_3 + 2\text{N}_2\text{PhOH} = \text{R}\cdot\text{CO}\cdot\text{C}(\text{N}_2\text{Ph})\cdot\text{N}_2\text{HPh} + 2\text{H}_2\text{O}.$
3. $\text{R}\cdot\text{CO}\cdot\text{CR}_1\cdot\text{N}\cdot\text{NHPh} + \text{N}_2\text{PhOH} = \text{N}_2\text{Ph}\cdot\text{CR}_1\cdot\text{N}_2\text{HPh} + \text{R}\cdot\text{COOH}.$

Their views regarding the constitution of methyl formazyl ketone are in agreement with those of v. Pechmann (preceding abstracts).

J. B. T.

Phenylhydrazidoisobutyronitrile and the Products of its Hydrolysis. By F. ECKSTEIN (*Ber.*, 25, 3319—3326).—The author has prepared phenylhydrazidoisobutyronitrile by adding the calculated quantity of acetone to an ethereal solution of phenylhydrazine and hydrogen cyanide, cooled to 0° , and subsequently heating the mixture for two hours on the water-bath in a closed vessel. He has also prepared the nitrile by Reissert's method (Abstr., 1884, 1152), and finds that the products are in both cases identical. From the first mode of formation, it therefore follows, in opposition to Reissert's views, that the nitrile has the symmetrical formula $\text{NHPh}\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{CN}$. When the nitrile is dissolved in absolute alcohol, and the solution saturated with hydrogen chloride as directed by Reissert (*loc. cit.*), the *amide*, $\text{C}_9\text{H}_{13}\text{N}_2\cdot\text{CONH}_2$, is obtained, a compound crystallising from benzene as a white, silky powder and melting at 117° . Reissert be-

lieved the last-named compound to be an imido-derivative. The author also finds that, contrary to Reissert's statement, phenylhydrazidoisobutyronitrile is converted into the amide just described, when it is allowed to remain in the cold with concentrated hydrochloric acid (10 parts) for 10—12 days; when the amide is boiled for a protracted period with concentrated hydrochloric acid (10 parts), it is quantitatively converted into phenylhydrazidoisobutyric acid (m. p. 165—166°), the *hydrochloride* of which crystallises from ether in four-sided, truncated pyramids, and melts at 182°. When phenylhydrazidoisobutyramide (Reissert's imide) is treated with tin and hydrochloric acid, ammonia is one of the products, as stated by Reissert; but the case is simply one of hydrolysis, and not of reduction, as phenylhydrazidoisobutyric acid is the other product. Phenylhydrazidoisobutyric acid is only partially attacked by tin and hydrochloric acid, aniline being identified as one of the products; but anilidobutyric acid was not recognised; the author therefore considers it desirable that Reissert should re-examine the products of this reaction. When phenylhydrazidoisobutyric acid is boiled with sodium hydroxide and animal charcoal, an acid, melting at 132°, is obtained; it is under investigation.

A. R. L.

Condensation of β -Benzoylphenylhydrazine with Aldehydes.

By G. MINUNNI (*Gazzetta*, 22, ii, 230—244).— β -Benzoylphenylhydrazine and pure benzaldehyde do not react at 200°, but with a certain sample of benzaldehyde containing some unknown impurity, reaction occurred readily at 125—130°. The mass first liquefies, and in 4—5 hours resolidifies; it is extracted on the water-bath with a little alcohol, and the residue dissolved in much hot alcohol. After filtration and concentration, a substance of the composition $C_{33}H_{26}N_4O_2$ is obtained in white flocks which melt at 218—219°; it probably contains two benzoyl groups. It is sparingly soluble in alcohol, ether, chloroform, and benzene, and readily soluble with partial decomposition in sulphuric acid, hydrochloric acid, or warm glacial acetic acid; in the first case benzoic acid is formed. With alcoholic potash, it yields a crystalline substance melting at 90—92°, which is still under examination.

β -Benzoylphenylhydrazine and pure benzaldehyde react readily in presence of anhydrous oxalic acid, but the condensation product described above could not be isolated from the mass; on heating a mixture of benzoylphenylhydrazine (5 grams), benzaldehyde (4 grams), and zinc chloride (2.5 grams) at 160—170°, the compound of the composition $C_{33}H_{26}N_4O_2$ is produced. The crystalline *diacetyl* derivative, $C_{33}H_{26}N_4O_2Ac_2$, melts at 257°. A *tetrabenzoyl* compound, of the formula $C_{33}H_{26}N_4O_2Bz_2 = C_{19}H_{16}N_4Bz_4$, was obtained; it forms white flocks, and melts at 168—169°. By the action of sodium nitrite and hydrochloric acid on the alcoholic solution of the condensation product, an oil is produced which readily decomposes with evolution of nitrous fumes, and, on treatment with potash, yields a substance which crystallises in needles and melts at 91—92°.

β -Benzoylphenylhydrazine and salicylaldehyde yield a crystalline product melting at 174°. The author is continuing the investigation.

W. J. P.

Action of Phenylhydrazine on some Isomeric Aldoximes.

By G. MINUNNI and G. CORSELLI (*Gazzetta*, 22, ii, 139—149).—Minunni and Caberti (Abstr., 1891, 1361) have shown that α - and β -benzaloxime and benzaldehyde give an α -hydrazone with phenylhydrazine: the authors now show that the normal hydrazone is always obtained with other α - and β -aldoximes. They consider that Hantzsch's investigations of the acetyl derivatives of the aldoximes (Abstr., 1891, 443) support Minunni's views of their constitutions (Abstr., 1891, 1354).

On heating α -paranisaldoxime, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NOH}$ (5.5 grams), with phenylhydrazine (4 grams) on the water-bath for five hours, ammonia is evolved, and, on cooling, the hydrazone is obtained as a crystalline mass. The same product is formed on heating β -paranisaldoxime, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$, with phenylhydrazine in molecular proportion on the water-bath.

α -Metanitrobenzaloxime melts at 122° (not at 118 — 119°), and gives an almost quantitative yield of the normal hydrazone on heating with phenylhydrazine. It separates from boiling alcohol in acicular red crystals melting at 123° . The same hydrazone is obtained on heating a concentrated alcoholic solution of metanitrobenzaldehyde and phenylhydrazine in molecular proportion, or by heating β -metanitrobenzaloxime and phenylhydrazine together.

α - or β -Cuminaldoxime, when similarly heated with phenylhydrazine, yields the normal hydrazone, which crystallises from alcohol in long, colourless needles, and melts at 124 — 125° . The same substance is formed, with development of heat, on mixing concentrated alcoholic solutions of cuminol and phenylhydrazine.

W. J. P.

New Method of determining the Structure of the Oximido-group in Ethers of the Oximes.

By G. MINUNNI and G. CORSELLI (*Gazzetta*, 22, ii, 149—164).—On treating the ether of an α -aldoxime with phenylhydrazine, a hydrazone and an α -substituted hydroxylamine are obtained, $\text{R}\cdot\text{CH}\cdot\text{NOR} + \text{NH}_2\cdot\text{NHPH} = \text{R}\cdot\text{CH}\cdot\text{N}\cdot\text{NHPH} + \text{NH}_2\cdot\text{OR}$. With the ethers of the β -oximes, a β -substituted hydroxylamine is formed, $\text{R}\cdot\text{CH}\cdot\text{N}\cdot\text{NR} + \text{NH}_2\cdot\text{NHPH} = \text{R}\cdot\text{CH}\cdot\text{N}\cdot\text{NHPH} + \text{R}\cdot\text{NH}\cdot\text{OH}$. These reactions afford a means of discriminating between α - and β -aldoximes.

α -Benzaloxime benzyl ether cannot be obtained free from benzyl chloride by Beckmann's method (Abstr., 1889, 607). In order to prepare a pure substance, a large excess of the sodium derivative of the oxime must remain in contact with benzyl chloride for many days; the benzyl ether is then precipitated with water and extracted with ether. On heating α -benzaloxime benzyl ether with phenylhydrazine in molecular proportion, a product is obtained which partly solidifies on cooling; after filtration, the oily filtrate is repeatedly heated, cooled, and filtered until no further separation of crystals occurs on cooling. The crystalline substance is the hydrazone of benzaldehyde, and melts at 156 — 157° ; on distilling the oil in a

current of steam, extracting the distillate with ether, and passing dry hydrogen chloride into the ethereal solution, crystalline laminæ of α -benzylhydroxylamine hydrochloride are precipitated.

On heating a mixture of α -benzaloxime methyl ether and phenylhydrazine in molecular proportion at 160 — 165° , in an oil-bath, the mass solidifies on cooling. The gaseous products are absorbed by hydrochloric acid; on evaporating this solution to dryness, dissolving the residue in alcohol, and adding ether, α -methylhydroxylamine hydrochloride melting at 146 — 147° separates. The solid product of the reaction, when washed with ether and crystallised from alcohol, is found to be benzaldehyde hydrazone; the ethereal washings contain small quantities of the unaltered methyl ether and phenylhydrazine.

α -Anisaloxime methyl ether reacts with phenylhydrazine at 150 — 160° with evolution of α -methylhydroxylamine, which is absorbed by hydrochloric acid. On cooling, the mass solidifies and consists of anisaldehyde hydrazone and a little resin.

A mixture of β -benzaloxime ethyl ether (which melts at 82 — 83° , not at 81 — 82°) and phenylhydrazine in molecular proportion liquefies at 80° , and then solidifies. On washing the mass with ether, the hydrazone of benzaldehyde remains undissolved, whilst the ethereal filtrate yields a precipitate of β -benzylhydroxylamine hydrochloride melting at 102° if dry hydrogen chloride is passed into it. The original benzyl ether is regenerated on treating the latter with benzaldehyde.

Ethers of β -aldoximes react much more readily with phenylhydrazine than those of the α -aldoximes.

W. J. P.

Action of Phenylhydrazine on the Benzoyl Derivatives of some α -Aldoximes. By G. MINUNNI and G. CORSELLI (*Gazzetta*, 22, ii, 164—173; compare preceding abstract).—On mixing ethereal solutions of benzoic chloride and α -benzaloxime in molecular proportion, *benzoyl- α -benzaloxime* separates; hydrogen chloride is evolved, and after some hours the deposit is collected, washed with ether, and crystallised from boiling absolute alcohol. It forms very beautiful, brilliant needles, melting at 101 — 102° ; the ethereal washings contain the benzoyl derivative and benzoic acid. A mixture of benzoyl- α -benzaloxime and phenylhydrazine in molecular proportion liquefies below 100° , and then solidifies to a mixture of benzoylphenylhydrazine and the hydrazone of benzaldehyde, which may be resolved by extracting the latter compound with cold benzene. The same products are formed if 2 mol. proportions of phenylhydrazine are employed to 1 of the benzoyl derivative.

Benzoyl- α -anisaldoxime, prepared in a similar manner to the preceding compound, crystallises from boiling dilute alcohol in shining, white laminæ melting at 109 — 110° . On heating it with phenylhydrazine in molecular proportion for several hours on the water-bath, ammonia is evolved, and the mass solidifies on cooling. When treated with benzene in the cold, the hydrazone of anisaldehyde dissolves, whilst benzoylphenylhydrazine remains.

Benzoyl- α -metanitrobenzaloxime crystallises in white laminæ; it melts at 161° , and separates on mixing ethereal solutions of equivalent

quantities of benzoic chloride and α -metanitrobenzaldoxime. On heating it with phenylhydrazine for several hours on the water-bath, ammonia is evolved, and the product crystallises out on cooling. Benzene extracts metanitrobenzaldehyde from the product, leaving a residue of benzoylphenylhydrazine.

W. J. P.

Formation of Benzonitrile from α -Benzaldoxime. By G. MINUNNI (*Gazzetta*, **22**, ii, 174—183).—In the preparation of benzoyl- α -benzaldoxime by the action of benzoic chloride on α -benzaldoxime in ethereal solution (see preceding abstract), the benzoyl derivative gradually separates as a white powder, hydrogen chloride being liberated after a time. If the ethereal solution containing the precipitate and the hydrogen chloride is allowed to remain for 8 to 10 days, the whole redissolves, and, on concentrating the solution, benzoic acid separates; on extracting the ethereal solution from which this has separated with sodium carbonate solution, and distilling off the ether, benzonitrile remains. This decomposition is due to the hydrogen chloride, for, on passing dry hydrogen chloride into ether containing benzoyl- α -benzaldoxime in suspension at -10° , the hydrolysis proceeds quantitatively.

On preparing acetyl- α -benzaldoxime by mixing ethereal solutions of α -benzaldoxime and acetic chloride in the requisite proportion and leaving the liquid to itself for 10 days, then agitating with soda, and adding hydrochloric acid to the solution, a precipitate of benzoic acid formed from the benzonitrile is obtained. The author proves that complete hydrolysis of the acetyl derivative occurs, with formation of acetic acid and benzonitrile, by preparing the acetyl- α -benzaldoxime in a freezing mixture, allowing the solution to remain for 20 days, and evaporating the ether at ordinary temperatures, when a residue of benzonitrile is obtained.

If an ethereal solution of acetyl- α -benzaldoxime, prepared from acetic chloride and α -benzaldoxime, is treated with dry hydrogen chloride at -10° , kept for a month at the ordinary temperature, and the ether then evaporated in a current of dry air, a crystalline residue is left. This, doubtless, contains an additive product of benzonitrile and hydrogen chloride, $\text{CCl}_2\text{Ph}\cdot\text{NH}_2$, for, on boiling it with aqueous ammonia in a reflux apparatus, a little benzonitrile remains undissolved, whilst benzamide and benzoic acid are obtained on extracting the ammoniacal solution with ether and concentrating the ethereal solution.

W. J. P.

Isomerism of Oximes. By G. MINUNNI (*Gazzetta*, **22**, ii, 191—212).—The author considers that he has demonstrated the futility of the stereochemical hypotheses offered by Auwers, V. Meyer, Hantzsch, and Werner for elucidating the isomerism of the oximes, his own theory being the only one which accords with the facts. He has shown that Hantzsch's first attack (*Abstr.*, 1891, 823) on his theory was based on misapprehension (*Abstr.*, 1892, 291), whilst the constitutional formulæ assigned by Claus are insufficient to explain the isomerism.

W. J. P.

Formation of Hydrogen Nitride (Azoimide) from Aromatic Azoimides. By E. NOELTING, E. GRANDMOUGIN, and O. MICHEL (*Ber.*, 25, 3328—3342; compare *Abstr.*, 1891, 1473).—*Paranitro-*

diazobenzeneimide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} < \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix}$, is prepared by adding a solution of diazotised paranitraniline to bromine (1 mol.), dissolved in a concentrated solution of potassium bromide (at least 1 mol.), when the *diazoperbromide* separates as a voluminous yellow precipitate, which, after being collected and washed with water at 0° , is added in small quantities, with stirring, to aqueous ammonia, kept cool meanwhile by the addition of ice. The compound is collected, washed, and crystallised from dilute alcohol, when it is obtained in bright yellow, lustrous leaflets; in the pure state, however, it is white, but soon becomes yellow on exposure to light. It is volatile with steam, melts at 74° , and is readily soluble in alcohol, ether, and benzene, but only very sparingly in hot water; on reduction with tin and hydrochloric acid, it yields paraphenylenediamine.

When paranitrodiazobenzeneimide (1 part) is added by degrees to a solution of potassium hydroxide (1 part) in absolute alcohol (10 parts), it dissolves, forming a deep-red solution; this is gently boiled on the water-bath for 48 hours, two-thirds of the alcohol distilled off, and the residue, after acidifying with dilute sulphuric acid, again distilled, when azoimide passes over with the alcohol and water vapour. The distillate is neutralised with alkali, evaporated to dryness, the residue dissolved in water, and the solution acidified and distilled, when an aqueous solution of azoimide, representing about 40 per cent. of the theoretical yield, is obtained. The operation is quite free from danger. A black carbonaceous mass (see below) is present in the residue from the first distillation; it is collected, and from the filtrate paranitraniline is isolated. The formation of the last-named compound accounts for the low yield of azoimide. (Compare also Tilden and Millar, *Proc.*, 1892, 215.)

On extracting the above-mentioned carbonaceous substance with boiling alcohol for several days, and crystallising it from the same solvent, Gattermann and Ritschke's parazophenetoil, melting at 136° (see *Abstr.*, 1890, 1120), is obtained; but paranitrophenol is apparently not a product of the action. This reaction may serve as a lecture experiment for the preparation of azoimide. When, for example, crude paranitrodiazobenzeneimide is heated on the water-bath for five minutes with 40 per cent. alcoholic potash, 25 per cent. of the calculated quantity of azoimide passes over.

Diorthobromoparanitrodiazobenzeneimide, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{N} < \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix}$, is prepared by diazotising diorthobromoparanitraniline (Wurster and Noelting, this *Journal*, 1875, i, 389), the mixture being kept in a cool place for six days, when it is poured into water at 0° , and bromine added; the precipitated *perbromide* is dropped into aqueous ammonia, and the *bromonitrodiazobenzeneimide* crystallised from dilute alcohol, and subsequently distilled with steam, when it is obtained quite colourless. It crystallises in long, white needles, becomes bluish-

green on exposure to light, melts at 68° , and is readily soluble in alcohol and benzene. On reduction with tin and hydrochloric acid, it gives the corresponding *paradiamine*, $C_6H_2Br_2(NH_2)_2$, which crystallises from hot water in long white, silky needles, melts at 138° , and yields an *acetyl* derivative melting at 108° .

When the pure dibromoparanitrodiazobenzeneimide is heated with 10 per cent. alcoholic potash, in the manner already mentioned, for about 40 hours, 80—85 per cent. of the theoretical amount of azoimide is obtained on distillation, and a solid carbonaceous mass remains in the flask; if this is pulverised and distilled with steam for several days, a compound melting at 190 — 195° slowly passes over. This, on treatment with hot alkali, is partially dissolved, and, on cooling, yellow needles separate consisting of the sodium derivative of diorthobromoparanitrophenol* (m. p. 141°); the *acetyl* derivative of this compound melts at 178.5° . The portion insoluble in alkali is crystallised from alcohol, and thus proves to be diorthobromoparanitraniline, whilst from the alcoholic mother liquors a compound melting at 105 — 115° is isolated. Finally, by extracting the carbonaceous substance, after all the volatile matter from it has been driven over with steam, tetrabromazoxyphenol (m. p. 155 — 156°) is obtained.

Metanitrodiazobenzeneimide is prepared in the same manner as its analogues; it crystallises from dilute alcohol in long, white needles, melts at 55° , is readily volatile with steam, and dissolves in alcohol, benzene, and ether, but is insoluble in water. It does not yield azoimide, even when heated with very concentrated alcoholic potash in a sealed tube.

Orthonitrodiazobenzeneimide, prepared in a similar manner to the para-compound, crystallises from a mixture of benzene and alcohol in long, broad needles, melts at 51 — 52° , and decomposes at 75 — 80° yielding a compound melting at 65 — 67° . It gives less than 30 per cent. of the theoretical amount of azoimide, which distils over, together with orthonitraniline, whilst a compound melting at 98° can be isolated from the carbonaceous residue remaining in the flask.

Orthoparadinitrodiazobenzeneimide, $C_6H_3(NO_2)_2 \cdot N \begin{smallmatrix} N \\ | \\ N \end{smallmatrix}$, is obtained from 2 : 4-dinitraniline as a brownish-red powder, but on crystallising it from alcohol it decomposes into a compound melting at 68° , and containing less nitrogen. It gives 50—55 per cent. of the theoretical quantity of azoimide on being heated with alcoholic potash, whilst 2 : 4-dinitrophenol is obtained from the non-volatile product of the reaction.

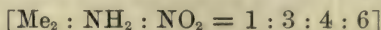
Metanitrorthodiazotolueneimide, $NO_2 \cdot C_6H_3Me \cdot N \begin{smallmatrix} N \\ | \\ N \end{smallmatrix}$, prepared from metanitrorthotoluidine (m. p. 128°), crystallises from dilute alcohol in lustrous, white needles, and melts at 73° . When heated with alcoholic potash, it yields about 30 per cent. of the theoretical amount of azoimide, together with metanitrorthotoluidine.

* The authors here note the interesting fact thus brought to light, namely, that dibromoparanitrophenol is volatile with steam, whereas paranitrophenol is non-volatile.

Orthonitroparadiazotolueneimide, obtained from orthonitroparaluidine (m. p. 77.5°), forms white, lustrous needles, and melts at $69-70^{\circ}$; it does not yield azoimide on treatment with alcoholic potash.

Paranitroorthodiazotolueneimide, prepared from paranitroorthotoluidine (m. p. 107°), crystallises in long, white, lustrous needles, melts at 68° , and does not give azoimide on treatment with alcoholic potash.

Metanitrodiazometaxylineimide, from nitrometaxylinidine,



(m. p. 123°), crystallises from dilute alcohol in thick, white needles, melts at 75° , and yields no azoimide on treatment with alcoholic potash.

It may be mentioned, finally, that diazobenzeneimide does not give azoimide on treatment with alcoholic potash, even under pressure, but tribromodiazobenzeneimide yields a small amount of azoimide. By this work it is seen that only those nitro-derivatives yield azoimide which contain the nitro-group in a para- or ortho-position relatively to the diazoimido-group.

A. R. L.

New Method of preparing Benzoic Anhydride. Formation of Dehydracetic acid from Acetic Chloride. By G. MINUNNI (*Gazzetta*, 22, ii, 213—217).—The reaction occurring between pyridine and acetic chloride, resulting in the conversion of the latter into dehydracetic acid, is explained by Feist on the assumption that dehydracetic acid is the product of the direct condensation of acetic chloride, and that the pyridine assists the reaction by combining with the liberated hydrogen chloride. This induced the author to examine the action of other acid chlorides on pyridine in order to obtain confirmation of this view.

On mixing ethereal solutions of benzoic chloride and pyridine, a white, deliquescent substance separates, which yields benzoic chloride and pyridine when treated with water. If no solvent is used, a slight rise in temperature is noted on mixing benzoic chloride and pyridine, an additive product being formed; whilst the liquid rapidly darkens and deposits a little pyridine hydrochloride. After a time, however, a considerable quantity of a white, deliquescent substance separates, and on treating this or the mother liquor with water, pure benzoic anhydride is precipitated, the pyridine remaining in the aqueous solution as hydrochloride. On adding water to the mixture half an hour after its preparation, 78 per cent. of the theoretical yield of pure benzoic anhydride may be obtained. This is, therefore, the most convenient and economical method known of preparing the anhydride.

The action of acetic chloride on pyridine may be explained in a manner similar to the above; the white substance first deposited is an additive product, and on treatment with water yields acetic anhydride, which at the moment of its formation condenses to form dehydracetic acid.

W. J. P.

Heptanaphthenic (Hexahydrobenzoic) acid. By V. MARKOVNIKOFF (*Ber.*, **25**, 3355—3366; compare *Abstr.*, 1892, 714, and *Aschan*, 1891, 1053, 1481; 1892, 847; and this vol., i, 33).—Benzoic acid was reduced by pouring a solution of it in a high-boiling alcohol (amyl, capryl, or octyl) upon melted sodium contained in a large round-bottomed flask, heating the mixture until all the sodium had disappeared, adding the equivalent amount of dilute sulphuric acid, removing the alcoholic solution, drying it by distilling off the water, and repeating the process 3—4 times with fresh sodium. The final product was then fractionated, and the pure acid obtained by freezing the fractions, pressing the crystals between filter-paper, and recrystallising from hot water. *Heptanaphthenic acid* melts at 28·5—29·5°, and boils at 234·5—235° under 750 mm. pressure. Its odour resembles that of both valeric acid and ethyl oxalate. The crystals deliquesce in the air, dissolve very readily in alcohol, ether, chloroform, benzene, and light petroleum, but only slightly in cold water, and are but little volatile with steam. The acid does not take up bromine, but decolorises permanganate rather rapidly.

The *sodium salt* forms crusts of transparent, efflorescent needles. The *calcium salt*, $(C_7H_{11}O_2)_2Ca + 5H_2O$, forms long needles; a basic salt was also obtained. The *barium salt*, $(C_7H_{11}O_2)Ba + 2\frac{1}{2}H_2O$, crystallises in bundles of small needles. The *magnesium salt* is very soluble, and forms crystalline crusts, which effloresce and form brilliant, white scales. The very characteristic *zinc salt* crystallises in brilliant scales or flattened needles, and is much more soluble in cold than in hot water. The *cadmium salt* is more soluble in hot water, but otherwise resembles the zinc salt. The *lead salt* forms a white precipitate which separates from water in small needles, or as a gelatinous crust. The *silver salt*, $C_7H_{11}O_2Ag$, forms a white precipitate, which, when dry, is but little affected by light. The *methyl salt* boils at 181—183° under 750 mm. pressure, and has a sp. gr. at 0°/0° = 1·0431, at 20°/20° = 0·9864; its odour resembles that of ethereal salts of fatty acids. The *amide*, $C_6H_{11}\cdot CONH_2$, crystallises in quadrangular plates, which group themselves in needles; it melts at 185—188°, and is but slightly soluble in water. When heptanaphthenic acid is heated at 290° with anhydrous copper sulphate, it is partly oxidised to benzoic acid, but some benzophenone is also formed.

Other unsaturated hydrobenzoic acids are also obtained when benzoic acid is reduced with sodium, but the study of them is left to *Aschan*. The latter's results respecting hexahydrobenzoic acid and its derivatives are criticised, and in cases of difference the author upholds his own figures, maintaining that he has worked with purer materials.

C. F. B.

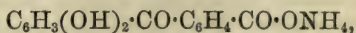
Separation of Phenyl dibromopropionic acid into its Optically Active Modifications. By L. MEYER, Jun. (*Ber.*, **25**, 3121—3123).—Freshly prepared and finely divided strychnine (1 mol.) is mixed with 20 times its weight of alcohol (92 per cent.), and phenyl dibromopropionic acid (1 mol.) dissolved in alcohol is added; a clear solution is obtained, which after a short time deposits

well-formed, colourless crystals of the *lævo*-acid. The *dextro*-acid remains in the mother liquor, and does not crystallise so well.

Strychnine lævo-phenyldibromopropionate, $C_{21}H_{22}N_2O_2, C_6H_5Br_2O_2$, begins to decompose at 80° , and is insoluble in water. The *lævo*-acid is obtained by rubbing the salt with very dilute hydrochloric acid until the insoluble residue shows no trace of strychnine. It is then crystallised from alcohol. It has all the properties of the inactive acid, but has a specific rotatory power $[\alpha]_D = -13.1$.

The *dextro*-acid is obtained from the mother liquor, and has a specific rotatory power $[\alpha]_D = +14.0$. E. C. R.

Sulphonephthaleïns. By C. C. BLACKSHEAR (*Amer. Chem. J.*, **14**, 455—473).—Commercial "saccharin" (50 grams) is boiled in a reflux apparatus for three quarters of an hour with dilute hydrochloric acid (1 to 12), the parasulphaminebenzoic acid which crystallises out on cooling is separated, the filtrate evaporated to dryness at 100° , and the residue is taken up with cold water and evaporated to crystallisation. The acid ammonium orthosulphobenzoate, $COOH \cdot C_6H_4 \cdot SO_2 \cdot ONH_4$, thus obtained (compare Remsen and Burton, *Abstr.*, 1890, 94; 15 grams), is heated with resorcinol (12 grams) at 170 — 175° , and stirred until water ceases to be evolved, when ammonium dihydroxybenzoylbenzenesulphonate,



separates in yellow, silky crystals, which gradually lose their colour on purification. The ammonium salt is converted into a *basic lead salt* by digestion with litharge in concentrated aqueous solution, and the acid liberated by hydrogen sulphide from the acetic acid solution of the lead salt. Dihydroxybenzoylbenzenesulphonic acid, with $3H_2O$ (compare Remsen and Linn, *Abstr.*, 1889, 710), crystallises in small, colourless, apparently monoclinic plates. The *barium salt*, with $6H_2O$, crystallises in small, colourless plates; the *calcium salt*, with $4H_2O$, and the *silver salt*, with $2H_2O$, in radial groups of colourless needles; and the *normal lead salt*, with $7H_2O$, in small, colourless rhombohedra or long needles. Attempts to form an ethyl salt and an acetyl derivative, and to displace the hydroxyl groups by chlorine by the action of phosphoric chloride, were unsuccessful. When the acid is heated with concentrated nitric acid, it yields trinitroresorcinol and orthosulphobenzoic acid. When heated with concentrated sulphuric acid at 160 — 180° , it is converted into sulphonefluoresceïn, which is collected, washed with cold water, dissolved in aqueous potassium hydroxide, and reprecipitated by dilute sulphuric acid.

JN. W.

The Indoxazen Group. By W. R. CATHCART, Jun., and V. MEYER (*Ber.*, **25**, 3291—3297).—In the course of their work on the oximes of substituted benzophenone, the authors have prepared considerable quantities of paradibromobenzophenone from parabromobenzoic chloride and bromobenzene; on one occasion, however, a compound was formed, which crystallised in small plates, melted at

142°, and contained 29 per cent. of bromine. It readily yielded an *oxime*, which was deposited from alcohol in colourless crystals melting at 156—159°.

Orthobromobenzophenone oxime has been previously described (Abstr., 1892, 992); it is prepared by the action of hydroxylamine on the ketone in alkaline solution at ordinary temperatures, or by heating the ketone with hydroxylamine hydrochloride in alcoholic solution at 130°; it crystallises from alcohol in large prisms, which melt at 76—132°; the anhydrous compound melts at 132—133°. No isomeric oxime could be detected.

Phenylindoxazen has also been described (*loc. cit.*); it boils at 331—336° with slight decomposition; its formation appears to be due to the presence of two negative (phenyl) groups linked to the same carbon atom, since the oximes of orthobromobenzaldehyde and of orthobromoacetophenone do not yield indoxazen derivatives; orthobromobenzoic hydrazone behaves in a similar manner (compare Russanow, next abstract).

Phenylindoxazen is not acted on by concentrated hydrochloric acid at 200°. A *dinitro-derivative*, $C_{13}H_7ON(NO_2)_2$, is obtained by adding powdered phenylindoxazen in small quantities to concentrated nitric acid, which is cooled with ice; the solution is quickly poured into a large volume of ice-cold water, and the deposited product purified by repeated crystallisation from glacial acetic acid; it is colourless, and melts at 239—241°.

No well characterised base could be obtained by the reduction of the above compound. J. B. T.

Indoxazen Derivatives. By A. RUSSANOW (*Ber.*, 25, 3297—3302).—It has been shown (preceding abstract) that the formation of indoxazen derivatives only proceeds when the group $C_6H_4Br\cdot CH:NOH$ is linked to a second negative group; orthobromophenylglyoxylic acid, $C_6H_4Br\cdot C(NO_2)\cdot COOH$, does not, however, yield indoxazencarboxylic acid, but decomposition products of this substance.

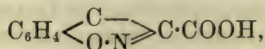
Orthobromobenzoic chloride, $C_6H_4Br\cdot COCl$, prepared from orthobromobenzoic acid and phosphoric chloride, is heated with 0.8 part of anhydrous silver cyanide in a sealed tube for 24 hours at 100°; the product is extracted with anhydrous ether, the solution evaporated, and the residual *cyanide* purified with light petroleum, from which it crystallises in yellow prisms melting at 62—64°.

Orthobromobenzoylformamide, $C_6H_4Br\cdot CO\cdot CONH_2$, is obtained by treating the cyanide with concentrated hydrochloric acid at the ordinary temperature; the reaction requires 24—48 hours for completion. The amide is soluble in about 5 parts of hot water, and crystallises in flat needles or plates melting at 136—137°. The yield is 85 per cent. of the cyanide employed.

Orthobromobenzoylformic acid, $C_6H_4Br\cdot CO\cdot COOH$, is formed by heating the amide (8.5 grams) dissolved in water (155 c.c.) with potassium hydroxide (2.1 grams) dissolved in water (45 c.c.), until evolution of ammonia ceases; the solution is acidified with hydrochloric acid, extracted with ether, and, after the removal of this, the

acid readily crystallises, and melts at 93—103°. The yield is 8 grams from the above quantities.

Orthobromisonitrosophenylacetic acid, $C_6H_4Br \cdot C(NO \cdot H) \cdot COOH$, is prepared from the preceding compound by the action of hydroxylamine in a feebly alkaline solution at the ordinary temperature; it crystallises from warm (not boiling) water in small, colourless needles, which melt at 162—164°, with decomposition. The impure oxime, on treatment with soda, yields resinous products, but on heating the crystallised compound for two hours with excess of soda (1 to 4), salicylic acid is obtained; in all probability the reaction proceeds in several stages. Indoxazencarboxylic acid,

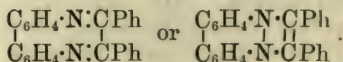


is first formed; from this carbonic anhydride is eliminated, and the resulting indoxazen, $C_6H_4 < \begin{smallmatrix} CH \\ O \end{smallmatrix} > N$, thus formed then changes into the nitrile, $OH \cdot C_6H_4 \cdot CN$, which, on hydrolysis, yields salicylic acid. The reaction is therefore analogous to the conversion of phenylisoxazole into benzoylacetate nitrile.

The fact that indoxazen is so unstable, whilst the phenyl derivative is not acted on by either acids or alkalis, is explained by the presence of a "wandering" hydrogen atom in the former compound.

J. B. T.

Orthodiamidodiphenyl. By E. TÄUBER (*Ber.*, **25**, 3287—3290).—Diorthamidodiphenyl combines with benzile in the same way as a true orthodiamine, and yields a compound of the formula



Diamidodiphenyl and benzile in molecular proportion are heated at 160—170° for 10—15 minutes, when a yellow, crystalline mass is obtained. It crystallises from acetic acid or alcohol in sulphur-yellow prisms, melts at 238°, distils unchanged in small quantities at the ordinary pressure, is indifferent to acids, and is easily soluble in ether, benzene, and phenol, sparingly so in alcohol, acetic acid, and light petroleum, and insoluble in water.

The reduction compound, $\begin{array}{c} C_6H_4 \cdot NH \cdot CHPh \\ | \\ C_6H_4 \cdot NH \cdot CHPh \end{array}$, is obtained by boiling the preceding compound with alcohol and excess of 3 per cent. sodium amalgam. It crystallises in colourless, lustrous aggregates of rhombohedra, or rhombic prisms, melts at 154°, is easily soluble in most solvents, insoluble in water, and has basic properties. It dissolves in dilute hydrochloric and sulphuric acids, and is reprecipitated on adding sodium acetate to the solution. With concentrated hydrochloric acid, it forms a sparingly soluble hydrochloride, which gives up its acid when washed with water. With nitrous acid, it yields a *nitroso-compound*, which melts at 208°, with evolution of gas, is insoluble in alcohol, and gives Liebermann's reaction. The base cannot be reconverted into the above yellow compound by weak oxidising

agents, and when treated with ferric chloride or chromic acid, it is completely destroyed.

E. C. R.

Oximes of certain Symmetrical Benzophenones. By W. R. CATHCART, Jun. (*Ber.*, 25, 3302—3303; compare this vol., i, 94).—Paradibromobenzophenone forms only one oxime melting at 151°; the oxime of paradimethylbenzophenone also exists in only one modification. *Paradimethoxybenzophenone* is prepared from paramethoxybenzoic chloride and methoxybenzene, and crystallises in colourless needles or plates which melt at 144—145°. The *oxime* is deposited from alcohol in colourless needles melting at 133—134°. No isomeric compound could be detected.

The following compounds appear to yield only one oxime:—

Meta- and para-dibromobenzophenone, paradichlorobenzophenone, paradiiodobenzophenone, paradimethylbenzophenone, paradimethoxybenzophenone. The corresponding para- and meta-*mono*-derivatives each yield two oximes; some of the ortho-compounds form only one oxime, whilst in the case of others the isolation of a second modification is a matter of difficulty.

J. B. T.

Benzileoximes. By G. MINUNNI and G. ORTOLEVA (*Gazzetta*, 22, ii, 183—190).— γ -Benzileoxime does not react with phenylhydrazine in a salt-water bath; reaction, however, occurs at 110—120°, ammonia is evolved, the mass liquefies, and, after a time, resolidifies. On washing the product with cold alcohol and crystallising the residue from boiling alcohol, minute, yellow needles of benziledihydrazone, melting at 223°, are obtained. The same product is formed on heating α -benzileoxime with phenylhydrazine at 120° until ammonia is no longer evolved; the mass is completely soluble in hot alcohol, but the dihydrazone separates after several days.

α -Benziledioxime (5 grams), when heated with phenylhydrazine (4.5 grams) at 150—160°, gives off ammonia, and, by treating the cooled mass with alcohol, unaltered dioxime and benziledihydrazone are obtained. On heating the dioxime (2 grams) with a large excess (10 grams) of phenylhydrazine at 170° for some hours, complete conversion into β -benziledioxime occurs; the latter then combines with the phenylhydrazine, forming a compound of the composition $\text{PhC:NH(OH)} > \text{N} \cdot \text{NHPh}$, which melts at 149°. On treating this with acids, it yields β -benziledioxime and phenylhydrazine.

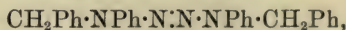
W. J. P.

α -Benzilephenylhydrazine and the Oxidation of the Hydrazones. By G. MINUNNI (*Gazzetta*, 22, ii, 217—230).— α -Benzilephenylhydrazine is readily formed on heating a mixture of benzyl chloride (1 mol.) and phenylhydrazine (2 mols.) at 120° for some hours. Water is then added, and the mass heated on the water-bath, when phenylhydrazine hydrochloride dissolves, whilst the substituted hydrazine separates as an oil. This is extracted with ether, and the ethereal solution shaken with dilute hydrochloric acid; on evaporat-

ing the aqueous solution on the water-bath and adding concentrated hydrochloric acid, the hydrochloride separates in white needles which yield the free base on treatment with potash. α -Benzilephenylhydrazine is an oil which does not crystallise on cooling, as has been stated. It decomposes and gives off ammonia on heating, and at 250° a yellowish-brown oil distils which gives a white, crystalline compound with benzaldehyde; this melts at 190—192°, and is sparingly soluble in ether.

α -Benzilephenylhydrazine hydrochloride crystallises from water in white needles, melts at 166—167°, and is much less stable than phenylhydrazine hydrochloride. It decomposes on heating with water, and, on treating its aqueous solution with sodium acetate solution, the free base separates. The *acetyl* derivative melts at 121—122°, and is readily soluble in hot xylene, giving a solution which dissolves sodium with evolution of hydrogen. The *benzoyl* derivative forms beautiful, white needles melting at 139—140°, and is readily soluble in the ordinary solvents.

On adding yellow mercuric oxide to a dilute chloroform solution of α -benzilephenylhydrazine, a slight rise of temperature occurs; after filtering and concentrating the solution, a *tetrazone*,



separates, and crystallises from alcohol in colourless laminae which melt with decomposition at 142°. The substance obtained by Michaelis and Phillips in needles melting at 109° could not be got. If a concentrated chloroform solution of α -benzilephenylhydrazine is treated with mercuric oxide, violent action occurs, and, on evaporating off the solvent and crystallising the product from alcohol, the tetrazone melting at 142° is obtained, together with a crystalline substance, more soluble in alcohol, which melts at 103—104°; the latter gave no satisfactory numbers on analysis:

On cautiously heating the hydrazone of benzaldehyde with yellow mercuric oxide on the water-bath, vigorous action occurs; the solution if filtered, concentrated, and left to crystallise, yields a substance which melts at 179—180°, and probably has the composition $\text{CHPh}\cdot\text{N}\cdot\text{NPh}\cdot\text{NPh}\cdot\text{N}\cdot\text{CHPh}$. It crystallises from benzene in beautiful, yellow needles, and is very sparingly soluble in hot alcohol. Mercuric oxide reacts with the hydrazone of metanitrobenzaldehyde, yielding a substance melting at 155°; this is still under examination.

Paranitrobenzile chloride does not act on phenylhydrazine in the cold, but, on heating, vigorous action sets in and a resin is obtained. Ethylene bromide only acts on phenylhydrazine on heating; at about 90°, reaction occurs with explosive violence, the flask being shattered. A mixture of monochloroacetal and phenylhydrazine gives off ammonia at 140°. On mixing ethereal solutions of chlorethyl oxide and phenylhydrazine, white laminae of an unstable substance melting at 121° are obtained.

W. J. P.

Derivatives of α - and β -Naphthylamine containing Asymmetrical Nitrogen and Carbon Atoms. By C. A. BISCHOFF

and A. HAUSDÖRFER (*Ber.*, **25**, 3263—3270).—*Diacetyldi- α -naphthylethylenediamine*, $C_2H_4(NAc \cdot C_{10}H_7)_2$, is obtained by warming a mixture of dinaphthylethylenediamine and acetic chloride. It crystallises in small, colourless tablets, melts at $239-241^\circ$, and is soluble in chloroform and hot acetic acid, and only sparingly so in other solvents.

Dimonobromacetyldi- α -naphthylethylenediamine is obtained by treating di- α -naphthylethylenediamine, dissolved in benzene, with bromoacetic bromide; it crystallises in colourless, four-sided prisms, melts at 215° with decomposition, is insoluble in water, ether, carbon bisulphide, acetone, light petroleum, dilute mineral acids, alkalis, and cold acetic acid, and sparingly soluble in chloroform and benzene, more so in hot alcohol.

Di- α -naphthylethylenediamine hydrobromide, $C_{22}H_{22}N_2Br_2$, is obtained as a bye-product in the preparation of the above and following compounds. It crystallises in faintly coloured aggregates, melts at $205-207^\circ$, is insoluble in ether and benzene, and easily soluble in hot chloroform and alcohol.

Di- α -bromopropionyl-di- α -naphthylethylenediamine, obtained in a similar way to the above compounds, crystallises in long, four-sided prisms, melts at 216° , and is easily soluble in carbon bisulphide, chloroform, and acetic acid. In one experiment, in which a large excess of acid bromide was employed in the formation of this compound, di- α -naphthylethylenediamine monhydrobromide, $C_{22}H_{21}N_2Br$, was obtained. This is also obtained by boiling the dihydrobromide with alcohol; it crystallises from alcohol in slender needles, melts at $236-237^\circ$, and is soluble in hot acetic acid.

Di- α -bromonormalbutyryldi- α -naphthylethylenediamine crystallises in long, four-sided prisms, and melts at $233-234^\circ$.

Di- α -bromisobutyryldi- α -naphthylethylenediamine melts at 197° , and resembles the preceding normal compound in crystalline form and solubility.

Di- β -naphthylcarbamide, $CO(NH \cdot C_{10}H_7)_2$, is obtained by adding carbonyl chloride dissolved in toluene to an ethereal solution of β -naphthylamine. It crystallises from nitrobenzene in slender needles, melts at 295° , and is insoluble in the ordinary solvents.

Oxaldi- β -naphthalide, $C_2O_2(NH \cdot C_{10}H_7)_2$, is obtained by heating a mixture of oxalic acid and β -naphthylamine at 265° . It crystallises in colourless tablets, melts at 276° , and is sparingly soluble in the ordinary solvents. When heated with 2—3 mol. proportions of alcoholic potash, it is decomposed into oxalic acid and naphthylamine. If however, only 1 mol. proportion of potash is employed, it yields an acid which is probably β -naphthyloxamic acid, $C_{10}H_7NH \cdot CO \cdot COOH$, and melts at 179° .

Succindi- β -naphthalide, $C_4H_4O_2(NH \cdot C_{10}H_7)_2$, is obtained by heating a mixture of β -naphthylamine (24 grams) and succinic acid (10 grams) at $190-200^\circ$ for one hour. The product, which contains β -dinaphthylamine (m. p. 172°), is extracted with water, acetic acid, and alcohol, and then crystallised from nitrobenzene. It is a colourless, microcrystalline substance, melts at 266° , and is insoluble in all the ordinary solvents, except concentrated sulphuric acid.

Diacetyldi- β -naphthylethylenediamine is obtained by heating di- β -naphthylethylenediamine with acetic anhydride at 150–175°. It crystallises from alcohol in small, colourless tablets, melts at 175–176°, and is insoluble in water and light petroleum.

Dimonobromacetyldi- β -naphthylethylenediamine is obtained, together with di- β -naphthylethylenediamine hydrobromide, by the action of bromacetic bromide on di- β -naphthylethylenediamine dissolved in benzene. It crystallises in colourless, microscopic needles, and melts at 144°.

Di- α -bromopropionyldi- β -naphthylethylenediamine crystallises with 1 mol. of benzene in thin, colourless prisms, and, after drying at 100°, melts at 196–197°.

Di- α -bromonormalbutyryldi- β -naphthylethylenediamine crystallises in slender, white needles, and melts at 180°.

Dibenzoyldi- β -naphthylethylenediamine is obtained, together with di- β -naphthylethylenediamine hydrochloride, by heating a mixture of di- β -naphthylethylenediamine (18 grams), benzene (300 grams), and benzoic chloride (30 grams) in a reflux apparatus for 15 hours. It crystallises in small, lustrous needles, melts at 202–203°, and is soluble in chloroform, hot acetic acid, carbon bisulphide, and benzene, sparingly soluble in acetone and cold benzene.

E. C. R.

Action of β -Naphthol on Formaldehyde. By H. HOSAEUS (*Ber.*, 25, 3213–3215).—When a tolerably concentrated solution of β -naphthol in glacial acetic acid is boiled with about an equal volume of commercial formaldehyde solution, *methylenedi- β -naphthol*, $\text{CH}_2(\text{C}_{10}\text{H}_6\cdot\text{OH})$, is formed. This crystallises in microscopic needles, melts at 188°, and is soluble in cold, dilute aqueous soda. The *diacetyl* derivative crystallises in needles melting at 214°.

Methylenedihydroxynaphthoic acid, $\text{C}_{23}\text{H}_{16}\text{O}_6$, was obtained by boiling a solution of β -hydroxynaphthoic acid with formaldehyde solution, with the addition of a few drops of dilute sulphuric acid. It crystallises in golden-yellow needles, insoluble in glacial acetic acid, alcohol, ether, benzene, and water. At 280° it blackens without melting.

L. T. T.

Terpenes from Resins. By O. WALLACH and T. RHEINDORFF (*Annalen*, 271, 308–311).—When copal is distilled, the oily distillate washed with soda and distilled with steam, a mobile liquid boiling at 40–350° is obtained. The lowest boiling fractions of this liquid seem to contain isoprene; the portions boiling at 154–164° consist principally of a hydrocarbon of the composition $\text{C}_{10}\text{H}_{16}$ which was proved to be pinene, and the fractions boiling at about 175° were found to contain dipentene (compare Friedburg, *J. Amer. Chem. Soc.*, 1890, 285).

The presence of pinene in the oil obtained by the dry distillation of commercial olibanum was also proved, whereas the product obtained in like manner from the hard elemi resin was found to contain dextrophellandrene.

The oil obtained by the dry distillation of colophony contains small quantities of pinene and dipentene.

F. S. K.

Sesquiterpenes. By O. WALLACH and W. WALKER (*Annalen*, **271**, 285—299).—Some of the sesquiterpenes, $C_{15}H_{24}$, behave in certain respects like some of the ordinary terpenes, and combine directly with 1 mol. H_2O , yielding crystalline compounds of the general formula $C_{15}H_{26}O$, which, when boiled with dilute acids, are reconverted into hydrocarbons by loss of 1 mol. H_2O .

Caryophyllene alcohol, $C_{15}H_{26}OH$, is best obtained by dissolving caryophyllene (25 grams), boiling at $250-260^\circ$, in a mixture of glacial acetic acid (1 kilo.), concentrated sulphuric acid (20 grams), and water (40 grams), and heating the solution for 12 hours on the water-bath. The mixture is then steam-distilled. At first, acetic acid and a mobile oil, having an ethereal odour, pass over, but towards the end of the operation, the alcohol, which is only slightly volatile, collects in the receiver, and gradually solidifies on cooling; it is first spread on porous earthenware, then distilled from a retort, and finally recrystallised from alcohol, from which it separates in well-defined, hexagonal, rhombic, hemihedric crystals melting at 96° . It boils at $287-289^\circ$ without appreciable decomposition, and dissolves freely in most of the ordinary organic solvents, but is only sparingly soluble in hot, and almost insoluble in cold, water; its vapours have a faint odour recalling that of pine needles. The *chloride*, $C_{15}H_{25}Cl$, prepared by treating the alcohol with phosphorus pentachloride, separates from ethyl acetate and from light petroleum in well-defined crystals, melts at 63° , and boils at $293-294^\circ$ without decomposition; it is readily soluble in hot, but more sparingly in cold, alcohol. The *bromide*, $C_{15}H_{25}Br$, is formed when the alcohol is treated with phosphorus tribromide, or with phosphorus and bromine in carbon bisulphide solution; it separates from alcohol in rhombic crystals, and melts at $61-62^\circ$. The *iodide*, $C_{15}H_{25}I$, prepared in like manner, crystallises in long, colourless needles or rhombic prisms, and melts at 61° ; it decomposes when heated. The *nitrate*, $C_{15}H_{25}O \cdot NO_2$, can be obtained by mixing the alcohol with a very small quantity of ethyl alcohol, and gradually adding excess of fuming nitric acid to the well-cooled mixture; on keeping for some time at the ordinary temperature, the ethereal salt is deposited in colourless needles, and a further quantity of the same substance is precipitated, but in an impure condition, on diluting the acid mother liquors. It crystallises in rhombic prisms, melts at 96° , and is soluble in alcohol, ether, and benzene; it is very stable, and is not acted on to any appreciable extent by boiling alcoholic potash or by a boiling alcoholic solution of sodium ethoxide, but, when heated with concentrated alcoholic potash at 150° , it is decomposed with formation of the alcohol. This ethereal salt seems also to be formed when a concentrated alcoholic solution of the chloride is treated with fuming nitric acid at a temperature below 70° .

All the compounds described above are optically inactive, and are extremely stable; the chloride seems not to be acted on by boiling aniline.

A *hydrocarbon* of the composition $C_{30}H_{50}$ is formed when the above-mentioned iodide is dissolved in ether and treated at the ordinary temperature with a large excess of sodium in the form of wire; it

boils at 225—230° (13 mm.), and solidifies on cooling to a brittle, transparent mass, which is almost insoluble in alcohol and glacial acetic acid, but readily soluble in ether; it separates from alcoholic ether in small, crystalline nodules, which sinter at 120°, but do not melt completely until the temperature rises to 135°.

Clovene, $C_{15}H_{24}$, is obtained when the alcohol described above is heated for 15 minutes almost to its boiling point with excess of phosphoric anhydride, the product distilled with steam, and again treated with phosphoric anhydride as before. It boils at 261—263°, and its sp. gr. is 0.930 at 18°; its refractive power is $[n]_D = 1.50066$ at 18°, from which the molecular refraction is calculated to be $M = 64.77$, whereas the calculated value for $C_{15}H_{24}$ is $M = 64.45$. This hydrocarbon cannot be converted into the crystalline alcohol from which it is derived, so that it must be regarded as different from caryophyllene.

An alcohol identical with the compound (m. p. 96°) described above can be obtained from the fraction of oil of copaiva boiling at 250—270° by the method already mentioned; that oil of cloves and oil of copaiva contain the same hydrocarbon is also proved by the fact that a crystalline nitrosochloride, $C_{15}H_{24}NOCl$, can be isolated from both the oils by the usual method; this compound is a colourless, sparingly soluble powder, melts at 161—163° with decomposition, and reacts very readily with piperidine, yielding an oily nitrolamine.

A *hydrocarbon*, which has in all probability the composition $C_{15}H_{28}$, is formed when dihydrochloros sesquiterpene (m. p. 118°) is heated with concentrated hydriodic acid at 200°; it boils at 257—260°, and behaves like a saturated compound; its sp. gr. is 0.872 at 18°, and its refractive power $[n]_D = 1.47439$, or $M = 67.09$, the calculated value for a saturated compound of the composition $C_{15}H_{28}$ being $M = 67.10$.

It is clear from the above experiments that some, at any rate, of the isomeric sesquiterpenes can be sharply distinguished from others; they may, in fact, be divided into two groups, according as they contain two or only one ethylenic linking. The best known representative of the first class is the widely distributed *lævorotatory* sesquiterpene, which is characterised by the crystalline additive product which it forms with two molecules of the halogen acids; the occurrence of this hydrocarbon in the oils of cubebs, savin, cadinum, betel, camphor, galbanum, patchouli, juniper, asafoetida, coto-bark, and olibanum has been proved. The author proposes the name *cadinene* for this sesquiterpene.

Cadinene contains two double linkings, and differs from caryophyllene in having a rather higher boiling point and in giving crystalline additive products with the halogen acids. Clovene differs from caryophyllene in not combining with water, and in not forming a crystalline nitrosochloride; it seems to contain only one ethylenic linking. The hydrocarbon which generally occurs with cadinene in ethereal oils, and which differs from the latter in not giving crystalline additive products with halogen acids, is also certainly not identical with caryophyllene. The sesquiterpene obtained from patchouli-camphor,

which is better termed patchouli alcohol, must also be regarded as a distinct compound, and is possibly related to cedrene, the sesquiterpene of cedar oil.

F. S. K.

Ethereal Oil of Paracoto Bark. By O. WALLACH and T. RHEINDORFF (*Annalen*, **271**, 300—308).—The ethereal oil which is obtained as a bye-product in the separation of the therapeutic constituents occurring in paracoto bark has been previously examined by Jobst and Hesse, according to whom it contains α -paracotene, $C_{12}H_{18}$; β -paracotene, $C_{11}H_{18}$; α -paracotol, $C_{15}H_{24}O$; and β - and γ -paracotol, $C_{28}H_{40}O_2$. A sample of the ethereal oil in question, which had been separated by distillation into "light" and "heavy" oil, was examined by the authors with the following results:—The fractions of lowest boiling point give, when shaken with sodium hydrogen sulphite, a very small quantity of a crystalline substance, which, when treated with dilute sulphuric acid, gives off an odour recalling that of benzaldehyde; this compound could not be characterised, as it is formed in such small quantities. When the portions of light oil which boil at 130 — 140° are saturated with a glacial acetic acid solution of hydrogen bromide, the mixture being well cooled, a crystalline substance is soon deposited; this compound melts at 121° , has the composition $C_{15}H_{26}Br_2$, and can be readily converted into a hydrocarbon, $C_{15}H_{24}$, which boils at 272° ; this hydrocarbon gives a crystalline dihydrochloro-derivative, $C_{15}H_{26}Cl_2$, which melts at 118° , and has a specific rotatory power of $[\alpha]_D = -33.5^\circ$ in chloroform solution; these facts prove that the hydrocarbon in question is identical with cadinene (compare preceding abstract).

The fractions of lowest boiling point obtained from the oil of coto bark also contained cadinene.

When the mother liquors from the crystalline dihydrobromo-derivative described above are treated with potash and submitted to steam distillation, an oil passes over; this is acted on readily by bromine in ethereal solution, with evolution of hydrogen bromide and formation of tribromomethyleugenol. The presence of methyleugenol in the coto bark oil is further proved by the fact that, when the "heavy" oil is oxidised with potassium permanganate it yields veratric acid (dimethoxybenzoic acid).

When methyleugenol is dissolved in light petroleum, and treated with an aqueous solution of sodium nitrite and dilute acetic acid, it is converted into a solid, unstable compound, which melts at about 125° , and has the composition $C_3H_5 \cdot C_6H_2(OMe)_2 \cdot N_2O_3$. F. S. K.

Essential Oil of Garlic (*Allium sativum*). By F. W. SEMMLER (*Arch. Pharm.*, **230**, 434—443).—Garlics were found to yield 0.09 per cent. of their weight of a yellow-coloured, optically inactive essential oil, which has the well known intense odour; it sp. gr. at 14.5° is 1.0525. It deposits a small quantity of crystals when cooled in a freezing mixture, does not contain oxygen, and decomposes when heated at 150° (compare Wertheim, *Arch. Pharm.*, 1891, 1). The oil was fractionally distilled under a pressure of 16 mm.

Fraction 1 (6 per cent.) consists of *allylpropyl bisulphide*, $C_3H_5S \cdot Spr$, a bright yellow oil of sp. gr. 1.0231 at 15° , boiling at $66-69^\circ$ (16 mm.), and having the odour of onions; it gives voluminous precipitates with mercuric and auric chlorides, which are sparingly soluble in alcohol, and, when treated with zinc-dust at 130° , yields a compound, $C_6H_{12}S$. It is decomposed by oxidising agents with the production of carbonic anhydride, oxalic acid, propionic and lower fatty acids, and sulphuric acid.

Fraction 2 (60 per cent.) is *diallyl bisulphide*, $S_2(C_3H_5)_2$, a light-yellow oil, having the odour of garlic; it is rendered colourless by distilling with a little potassium, when it passes over at $78-80^\circ$ (16 mm.). It has a sp. gr. at $14.8^\circ = 1.0237$, and on reduction with zinc-dust, yields a compound, $C_6H_{10}S$, which boils under the ordinary pressure at $135-139^\circ$; it also reacts with potassium, decomposes into carbonic anhydride, oxalic, formic, and acetic acids, on oxidation with nitric acid, combines with halogens, and does not react with mercuric oxide, even at 100° .

Fraction 3 (20 per cent.), representing the portion passing over between 112° and 122° (16 mm.), has the empirical formula $C_6H_{10}S_2$, its sp. gr. at 15° being 1.0845; it yields the compound, $C_6H_{10}S$, when heated with zinc dust.

Fraction 4 (10.5 per cent.) consists of the residue boiling above 122° (16 mm.); it decomposes if the distillation is continued. On analysis, values were obtained approximating to those required by the formula $C_6H_{10}S_4$.

Oil of garlic contains, therefore, neither allyl sulphide, as stated by Wertheim (*loc. cit.*), nor a sesquiterpene, as stated by Beckett and Wright (*Jahresb.*, 1878, 398).
A. R. L.

Note.—The sesquiterpene, to which the author refers, was obtained by Church from oil of cloves, and examined by Beckett and Wright (this Journal, 1876, i, 6). It is erroneously stated in the *Jahresbericht* (*loc. cit.*) that the terpene was isolated from oil of garlic (Knoblauchöl).
A. R. L.

Essential Oil of Onion (*Allium cepa*, L.). By F. W. SEMMLER (*Arch. Pharm.*, 230, 443—448).—Onions yield 0.005 per cent. of their weight of a dark-brown, essential oil, which does not contain oxygen, has a sp. gr. at $8.7^\circ = 1.041$, and exhibits a rotation of -5° in a 100 mm. tube; a small quantity of crystals separate on cooling it in a freezing mixture. As it decomposes when distilled at the ordinary pressure, it was fractionated under a pressure of 10 mm.

The main portion of the oil consists of a compound, $C_6H_{12}S_2$, an oil of sp. gr. 1.0234 at 12° , which boils at $75-83^\circ$ (10 mm.), and is converted into the compound $C_6H_{14}S_2$ on treatment with potassium; this new compound boils at $68-69^\circ$ (10 mm.), and seems to be present in small quantity in the original oil. The compound $C_6H_{12}S_2$ is converted by zinc-dust into a monosulphide, $C_6H_{12}S$ (b. p. 130°). A small quantity of a substance was isolated from the fractions boiling above 100° (10 mm.), and appears to be identical with one of the

compounds obtained from oil of asafoetida. The residue boiling above 125° (10 mm.) contains a higher sulphide, and gives the compound $C_6H_{12}S$ on reduction with zinc-dust. Neither allyl sulphide, nor a sesquiterpene, were present.

A. R. L.

Menthylamine. By O. WALLACH and M. KUTHE (*Ber.*, **25**, 3313—3316).—The preparation of menthylamine from menthone and ammonium formate has been described by Wallach (*Abstr.*, 1892, 500), whilst Andres and Andréeff obtained menthylamine by the reduction of menthone oxime (*Abstr.*, 1892, 723). A comparison of the two substances, and of some derivatives, shows that whilst the bases have almost identical boiling points, they and their derivatives have opposite and equal optical activities, the first being dextrorotatory, the second lævorotatory. The compound prepared from ammonium formate always contains a little lævorotatory menthylamine. The following table gives the melting points of the chief derivatives of these compounds; column I refers to Wallach's compound, column II to Andres and Andréeff's:—

	I.	II.
Menthylamine hydrogen chloride, $C_{10}H_{19} \cdot NH_2 \cdot HCl$	M. p. 189°	Unmelted at 28°
Formylmenthylamine, $C_{10}H_{19} \cdot NH \cdot COH$	„ $117-118^{\circ}$	M. p. 102°
Acetylmenthylamine, $C_{10}H_{19} \cdot NHAc$	„ 168°	„ 144°
Propionylmenthylamine, $C_{10}H_{19} \cdot NH \cdot COEt$	„ 151°	„ 89°
Butyrylmenthylamine, $C_{10}H_{19} \cdot NH \cdot COPr$	„ 106°	„ $76-77^{\circ}$
Phenylmenthylthiocarbamide, $C_{10}H_{19} \cdot NH \cdot CS \cdot NHPh$	„ $178-179^{\circ}$	„ 135°

J. B. T.

Constituents of Oil of Thuja. By O. WALLACH (*Annalen*, **272**, 99—122).—Thuja oil, which, according to Jahns (*Arch. Pharm.*, **221**, 748), consists principally of thujol, an isomeride of camphor, can be separated by distillation into three principal fractions boiling at $160-190^{\circ}$, $190-200^{\circ}$, and $200-215^{\circ}$ respectively. The fraction of lowest boiling point contains pinene, probably also ethereal salts of acetic acid. The intermediate fraction, which forms the principal portion of the oil, consists of a mixture of levo-fenchone and thujone, which can be only partially separated by repeated fractional distillation. The fraction of highest boiling point has not yet been investigated.

Levo-fenchone, $C_{10}H_{16}O$, is easily obtained in a pure state by boiling the fraction distilling at $190-195^{\circ}$ with concentrated nitric acid in order to oxidise the thujone, and then distilling the unchanged fenchone with steam. It melts at 5° , boils at $192-194^{\circ}$, and its sp. gr. is 0.948 at 20° ; its specific rotatory power is $[\alpha]_D = -66.94^{\circ}$, and its refraction $[n]_D = 1.46355$ or $M = 44.21$, the calculated value being $M = 44.11$; these properties show it to be the optical isomeride of the dextro-fenchone previously described (*Abstr.*, 1891, 218 and 1086; 1892, 1237).

Levo-fenchyl alcohol, $C_{10}H_{17}OH$, prepared by reducing the ketone with sodium and alcohol, has a specific rotatory power $[\alpha]_D = 10.36^\circ$.

Levo-fenchone oxime, $C_{10}H_{16}NOH$, the *nitrile*, $C_9H_{13}CN$, the α -*iso-oxime*, $C_{10}H_{17}NO$, the β -*iso-oxime*, *levo-fenchylamine*, and some of its derivatives, were prepared and found to be identical, except as regards the sign of their rotatory power, with the corresponding derivatives of *dextro-fenchone* (*loc. cit.*).

A number of the racemic modifications of the derivatives of fenchone were obtained by the combination of the two active modifications; in the following table, the melting points of the active and inactive compounds are given:—

	Active.	Inactive.		Active.	Inactive.
Fenchyl alcohol...	40°	33—35°	Benzylidenefenchyl-		
Fenchone oxime...	160—161	158—160	amine.....	42°	liquid
α -Iso-oxime.....	114—115	98—99	Hydroxybenzylidene-		
β -Iso-oxime.....	137	160—161	fenchylamine.....	95	64—65°
			Phenylfenchylthio-		
			carbamide.....	152—153	169—170

Thujone, $C_{10}H_{16}O$, boils at a higher temperature than fenchone, but it is doubtful whether it has yet been obtained free from the latter. It combines with hydroxylamine yielding an oily oxime, and, on reduction with sodium and alcohol, it is converted into an alcohol of the composition $C_{10}H_{18}O$, boiling at 210—212°.

Thujylamine is obtained, together with fenchylamine, when crude thujone is heated with ammonium formate and the product hydrolysed; it is purified by means of its hydrochloride, which is insoluble in ether, that of fenchylamine being soluble; it boils at 198—199°. The *hydrochloride*, $C_{10}H_{19}N.HCl$, and the *nitrate* are readily soluble in water, but the *sulphate* is only sparingly soluble; the *platinochloride* has the composition $(C_{10}H_{19}N)_2.H_2PtCl_6$. When the hydrochloride is submitted to dry distillation, it is decomposed into ammonium chloride and a hydrocarbon of the composition $C_{10}H_{16}$, which is named *thujene*; this compound boils at 172—175°, its sp. gr. is 0.840 at 20°, and its refractive power is $[n]_D = 1.4761$.

α -*Thujaketonic acid*, $C_{10}H_{16}O_3$, or β -*thujaketonic acid*, $C_{10}H_{16}O_3$, is produced when thujone is oxidised with potassium permanganate, but the conditions which lead to the formation of one or the other compound have yet to be determined.

The α -acid crystallises from water in well-defined, transparent plates, melts at 75—76°, and is completely soluble in about 40 parts of boiling water; when heated, it is converted into a ketone with evolution of carbonic anhydride. The *silver salt*, $C_{10}H_{15}O_3Ag$, is only sparingly soluble in cold water. The *oxime*, $C_{10}H_{17}NO_3$, separates from alcohol and water in crystals, melts at about 168° with decomposition, and is only sparingly soluble in ether, and very sparingly in water.

The β -acid crystallises from boiling water in small needles, melts at $78-79^\circ$, and is completely soluble in about 70 parts of boiling water. The *silver salt*, $C_{10}H_{15}O_3Ag$, separates from boiling water, in which it is only very sparingly soluble, in crystals. The *oxime*, $C_{10}H_{17}NO_3$, melts at $104-106^\circ$, and separates from dilute alcohol in needles.

Methyl heptylene ketone, $C_9H_{16}O$, is formed, together with a smaller quantity of a liquid acid and carbonic anhydride, when β -thujaketonic acid is submitted to dry distillation. It boils at $184-186^\circ$, and is volatile with steam; its sp. gr. is 0.854 at 20° , and its refraction $[n]_D = 1.44104$. It combines directly with bromine, and yields an oxime on treatment with hydroxylamine; it is readily oxidised by potassium permanganate, and, on reduction with sodium and alcohol, it is converted into an alcohol which has an agreeable odour recalling that of linalol. When warmed with zinc chloride, it is converted into an unsaturated hydrocarbon of the composition C_9H_{14} , which yields solid nitro-derivatives on treatment with concentrated nitric acid.

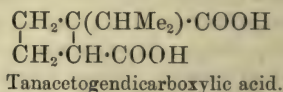
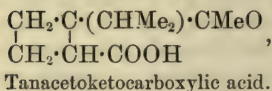
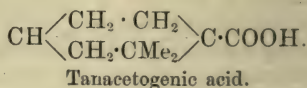
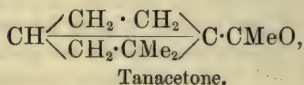
F. S. K.

Camphors containing the Group $CO \cdot CH_3$. By F. W. SEMMLER (*Ber.*, 25, 3343—3352).—*Tanacetone*, $C_{13}H_{16}O = C_8H_{13} \cdot CO \cdot CH_3$, is contained in the oils of tansy (*Tanacetum vulgare*), absinth, sage, and thuja, usually to the extent of about 50 per cent.; it may be separated by means of its crystalline sodium hydrogen sulphite compound or its oxime. It is an oil boiling at 84.5° under 13 mm. pressure, dissolves in ether but not in water, has a sp. gr. 0.9126 at 20° , its refractive power $[n]_D = 1.4495$, and its rotation is $+38^\circ 30'$ in a column 200 mm. long. It appears to have the formula given at the end of this abstract. When reduced with sodium, it yields *tanacetyl alcohol*, $C_8H_{13} \cdot CHMe \cdot OH$, which boils at 92.5° under 13 mm. pressure, has a sp. gr. of 0.9249 at 20° , and a refractive power $[n]_D = 1.4635$. This substance behaves like a saturated compound, bromine forming substitution, and not additive derivatives; phosphoric chloride converts it into *tanacetyl chloride*, boiling at 72° under 10 mm. pressure. With hydroxylamine, tanacetone yields *tanacetoxime*, $C_8H_{13} \cdot CMe \cdot NOH$, which melts at 51.5° and boils at $135-136^\circ$ under 20 mm. pressure. When reduced with sodium, the oxime yields *tanacetylamine*, $C_8H_{13} \cdot CHMe \cdot NH_2$, which boils at 80.5° under 14 mm. pressure, has a sp. gr. of 0.8743 at 20° , and a refractive power $[n]_D = 1.462$; it behaves like a fatty amine in taking up carbonic anhydride from the air. Its hydrochloride, $C_{10}H_{19}N \cdot HCl$, is insoluble in ether; when distilled, it yields *tanacetene*, $C_{10}H_{16}$, which boils at $60-63^\circ$ under 14 mm. pressure, has a sp. gr. of 0.8408 at 20° , and a refractive power $[n]_D = 1.476$; it appears to be a terpene with two ethylene linkings.

When tanacetone is shaken with alkaline hypobromite, bromoform is liberated (proof of $CO \cdot CH_3$ group) and *tanacetogenic acid* formed. This is an oil which boils at 113.5° under 15 mm. pressure, and forms needles when placed in a freezing mixture; it behaves like a saturated compound; its *silver salt*, $C_9H_{13}O_2Ag$, is somewhat sensitive to light. If tanacetone is oxidised with permanganate, *tanacetoketocarboxylic*

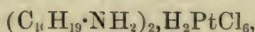
acid is formed; this crystallises from light petroleum in needles melting at 78° , but from hot water usually in rhombohedral plates melting at 74.5° . These two varieties are probably geometrically isomeric, and are identical with the β - and α -thujaketonic acids of Wallach (preceding abstract). The *silver salt*, $C_{10}H_{15}O_3Ag$, forms a white precipitate; the *oxime*, $C_{10}H_{15}O_2:NOH$, exists in two varieties, α - melting at 168.5° and β - at 103° , prepared respectively from the acids melting at 74.5° and 78° . If the acid itself is dissolved in soda and bromine added, bromoform and *tanacetogendicarboxylic acid* are formed. This acid melts at 141.5° , but a geometrically isomeric variety, melting at a much lower temperature, appears also to exist. It yields a *silver salt*, $C_9H_{12}O_4Ag_2$, and, like all orthodicarboxylic acids, an anhydride when heated with acetic anhydride. This *anhydride*, $C_9H_{12}O_3$, forms white needles, melts at 55° , and boils at 171.5° under 16 mm. pressure. When the acid is fused with potash, pimelic acid is formed, but if distilled with soda-lime, it yields *tanacetophorone*, $C_8H_{12}O$, an oil with an odour like that of camphorone. This boils at $89-90^{\circ}$ under 13 mm. pressure, and has a refractive power $[n]_D = 1.4817$; it appears to be a ketone.

The formulæ assigned to the above-mentioned compounds are as follows:—



C. F. B.

Campholamine. By G. ERRERA (*Gazzetta*, **22**, ii, 109—122; compare Abstr., 1892, 1345).—*Campholamine*, $C_{10}H_{19}NH_2$, is prepared by saturating a boiling solution of campholonitrile in absolute alcohol with sodium, adding water, acidifying the solution with hydrochloric acid, and distilling in a current of steam to eliminate any unchanged nitrile. On rendering the solution alkaline with soda, and again distilling in a current of steam, the pure amine is obtained as a colourless oil lighter than water. It has an alliaceous, ammoniacal odour, and boils at 210° , but is readily volatile at ordinary temperatures. It absorbs carbonic anhydride from the air, forming a white, crystalline substance, which is probably *campholyl camphocarbamate*, $C_{10}H_{19} \cdot NH \cdot CO \cdot NH_2(OH) \cdot C_{10}H_{19}$. The amine is insoluble in alkalis, and sparingly soluble in water. The *hydrochloride*, $C_{10}H_{19} \cdot NH_2 \cdot HCl$, crystallises in colourless, silvery laminæ, soluble in water, and decomposes on heating. The *platinochloride*,



separates from alcohol in beautiful yellow laminæ. The *nitrate* is sparingly soluble in cold water, and forms silvery scales; it melts

with decomposition at 210° or 220° , according as the heating is slow or rapid. The *benzoyl* derivative crystallises from light petroleum in lustrous, colourless needles, melting at 98° .

Phenylcampholylthiocarbamide, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{19}$, is obtained by the interaction of ethereal solutions of campholamine and phenylthiocarbimide in molecular proportion. The carbamide separates immediately, and crystallises from dilute alcohol in colourless needles melting at 117 — 118° ; it is very soluble in alcohol, sparingly so in light petroleum, and insoluble in water.

Campholylcamphelylcarbamide, $\text{C}_{10}\text{H}_{12}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_9\text{H}_{17}$, is obtained by the action of campholamine on camphelylthiocarbimide in ethereal solution. It separates from dilute alcohol in lustrous, colourless needles melting at 259 — 260° ; it is very soluble in alcohol, sparingly so in ether, and insoluble in water.

On mixing hot aqueous solutions of silver nitrite and campholamine hydrochloride in molecular proportion, campholamine nitrite is formed, and on prolonged boiling with water, decomposes with evolution of nitrogen, and formation of an oil, which distils with the steam. The oil, after washing with dilute hydrochloric acid, is dried, and on fractional distillation yields two products, boiling at 160 — 165° and 200 — 205° respectively. The former, *campholene*, $\text{C}_{10}\text{H}_{18}$, is a mobile, colourless liquid of pleasant odour, which immediately reduces permanganate or bromine water. It boils at 163° , and is possibly identical with the hydrocarbon obtained by Weyl (*Ber.*, **1**, 96) by heating camphor with hydriodic acid. The substance boiling at the higher temperature is *campholyl alcohol*, $\text{C}_{10}\text{H}_{19}\cdot\text{OH}$; it is a colourless, slightly oily liquid, of pleasant, aromatic odour, and boils at 203° .

The author terms the hydrocarbon $\text{C}_{10}\text{H}_{18}$ *campholene*, identifying it with the campholic series; its lower homologue, C_9H_{16} , which is ordinarily termed campholene, the author prefers to call *camphelene*. The constitutional formulæ involved in the above reactions are discussed, but no definite result is arrived at.

Campholenamide is optically active, and melts at 127 — 128° . In 5—9 per cent. solutions $[\alpha]_D = -3.8^{\circ}$ approximately.

W. J. P.

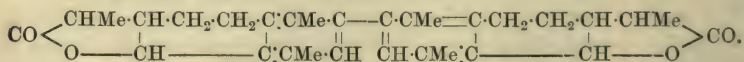
Derivatives of Amethylcamphonitroketone. By P. CAZENEUVE (*Bull. Soc. Chim.* [3], **7**, 327—331; compare Abstr., 1892, 999 and 1085).—The *sodium* derivative of amethylcamphonitroketone, $\text{NO}_2\cdot\text{C}_9\text{H}_{10}\text{NaO} + 2\text{H}_2\text{O}$, forms red, micaceous scales, is soluble in water and in alcohol, and deflagrates on heating. The *ethyl* derivative, $\text{NO}_2\cdot\text{C}_9\text{H}_{10}\text{EtO}$, obtained by heating the potassium compound with excess of ethyl iodide in a sealed tube at 130° , is a syrupy liquid not miscible with water, but soluble in alcohol and ether; when treated with sodium ethoxide, it decomposes into ethyl ether and the sodium derivative of the nitro-ketone, but if dissolved in toluene and heated with sodium, it is converted into an amorphous compound $\text{NO}_2\cdot\text{C}_9\text{H}_9\text{NaEtO}$. The *acetyl* derivative, $\text{NO}_2\cdot\text{C}_9\text{H}_{10}\text{AcO}$, is obtained by adding acetic chloride to the anhydrous sodium or potassium derivative, or by heating them with acetic anhydride at 150° ; the product is triturated with cold alkali and crystallised from alcohol; it forms six-sided tables, melts at 65° , explodes at 250° , and decom-

poses into ethyl acetate and the sodium derivative of the nitro-ketone on treatment with sodium ethoxide. When the acetyl derivative is dissolved in toluene and treated with sodium, the compound $\text{NO}_2 \cdot \text{C}_9\text{H}_9\text{NaAcO}$ is formed; it has the colour of mercuric iodide, dissolves in water, but is gradually decomposed by it, and is more soluble in alcohol. A compound soluble in alkalis is also formed in this reaction; it is perhaps a pinacone. A. R. L.

Tinctorial Properties of Amethylcamphonitroketone. By P. CAZENEUVE (*Bull. Soc. Chim.* [3], 7, 331—332).—Amethylcamphonitroketone (preceding abstract) dyes wool or silk without a mordant, not, however, in an alkaline bath; cotton mordanted with tannin also fixes the compound. The compound contains the chromophoric group NO_2 , but no salt-forming (auxochromic) group. The group CH_2 is of an acidic nature by virtue of its position between the groups NO_2 and CO (see Abstr., 1892, 1085), and the tinctorial properties of the nitroketone are, perhaps, to be ascribed to this circumstance. A. R. L.

Coniferin. By E. O. v. LIPPMANN (*Ber.*, 25, 3220—3221).—The author has isolated coniferin from *Scorzonera hispanica*. Vanillin appeared also to be present in small quantities, but could not be separated from other aldehydic substances present. L. T. T.

Reduction Products of the Santonins, Santonone, and Isosantonone. By G. GRASSI-CRISTALDI (*Gazzetta*, 22, ii, 123—129; compare Abstr., 1892, 869).—*Santonone*,



This lactone is prepared by gradually adding zinc-dust (5—6 grams) to a hot solution (300 c.c.) of santonin (10 grams) in acetic acid (50 per cent.), preferably in presence of a little platinum tetrachloride. After six hours' heating, the crystalline deposit is collected, washed with water, dried, and extracted with boiling alcohol in a reflux apparatus. Santonone separates from the alcoholic solution on cooling. It forms silky, white needles melting at 223° ; it is very soluble in benzene, less so in hot alcohol, ether, or dilute acetic acid, and insoluble in water. It is optically active in solution; for a 2 per cent. solution in benzene $[\alpha]_D = +129.46^\circ$; its molecular weight, as determined by the cryoscopic or the boiling-point method in benzene solution, is normal.

Santononic acid, $\text{C}_{30}\text{H}_{38}\text{O}_6$, is a bibasic acid, obtained by boiling a solution of santonone in dilute barium hydroxide for 10 hours. After precipitating the excess of barium by carbonic anhydride, and filtering, the acid is precipitated by acetic acid, collected, washed, dissolved in absolute alcohol, and allowed to crystallise. It is thus obtained in beautiful, micaceous laminæ melting at $215\text{--}216^\circ$ with decomposition. It is very soluble in ethyl or methyl alcohol, sparingly so in ether, benzene, ethyl acetate, or chloroform, and insoluble in water. In a 1 per cent. alcoholic solution, it has the specific

rotatory power $[\alpha]_D = +37.08^\circ$ at 20° . The aqueous solution of its ammonium salt gives white precipitates with zinc, mercuric, lead, or cadmium salts; precipitates are produced on heating with manganese, nickel, or cobalt salts. Copper sulphate gives a blue precipitate. On dehydration with acetic anhydride, the acid yields santonone.

Isosantonone, $C_{30}H_{34}O_4$, an isomeride of santonone, is obtained by slowly adding concentrated sulphuric acid to a cooled, concentrated alcoholic solution of santonic acid. It is a white substance melting with decomposition at 280° ; it is very soluble in chloroform, sparingly in ethyl acetate, acetic acid, ether, ethyl or methyl alcohol, and benzene, and insoluble in water or light petroleum. It gives a normal molecular weight by the cryoscopic method in acetic acid solution, and in a 1 per cent. glacial acetic acid solution has the specific rotatory power $[\alpha]_D = -264.7^\circ$. It is also formed on heating a solution of santonic acid in dilute alcohol, water, or ether on the water-bath. The glacial acetic acid solution of santonic acid is laevorotatory owing to partial conversion into santonone; the laevorotation gradually increases. Isosantonone may be also prepared by slowly adding zinc-dust to a heated solution of santonic acid (10 grams) in 70 per cent. acetic acid (300 c.c.); a little platinum tetrachloride is also added. After six hours' heating on the water-bath, the isosantonone is precipitated from the solution by water.

Isosantononic acid, $C_{30}H_{38}O_6$, an isomeride of santonic acid, is prepared from isosantonone in the same way as santonic acid is obtained from santonone. It is a white powder which melts at $167-168^\circ$. On heating at 200° , it is reconverted into isosantonone; the same change occurs slowly at 100° . It is optically active in solution; in a 1 per cent. alcoholic solution $[\alpha]_D = -40.39^\circ$. Solutions of its salts are very unstable, decomposing with separation of the lactone; the silver salt, $C_{30}H_{36}O_6Ag_2$, is a white, granular powder.

There is a very marked analogy in properties, indicating constitutional similarities, between the hyposantonines and the santonones.

W. J. P.

Santonin. By J. KLEIN (*Arch. Pharm.*, **230**, 499—513).—Constitutional formulæ for santonin have been proposed by Cannizzaro (*Abstr.*, 1886, 73), and recently by Grassi-Cristaldi (*Ber.*, **24**, Ref. 908), which represent it as a hydrogenised naphthalene derivative. The author points out, however, that in the production of naphthalene derivatives from santonin, three carbon atoms are invariably removed, which may exist in the compound as an isopropyl group. Taking into account this possibility, together with the fact that cineol occurs in wormseed together with santonin, it seems not improbable that santonin may be related to the terpenes, and be a derivative of a hydrocarbon, $\begin{array}{c} CH_2 \cdot CMe \cdot CH \cdot CH_2 \cdot CH_2 \\ | \qquad | \qquad | \\ CH_2 \cdot CMe \cdot CH \cdot CH_2 \cdot CH \cdot CHMe_2 \end{array}$, which may be named *santogenene*. Santonic acid would then be *keto-hydroxysantogenenic acid* and santonin *keto-hydroxysantogenenic lactone*.

Dihydroxysantogenenic acid, $OH \cdot C_{13}H_{18}(CH \cdot OH) \cdot COOH$, is obtained by the action of sodium on an alcoholic solution of santonin; it forms white, pointed crystals, melts at $162-164^\circ$, and is readily soluble in

alcohol and ether. The *silver* salt is a white, crystalline precipitate which blackens on warming with water.

Hydroxysantogenenic acid, $\text{OH} \cdot \text{C}_{13}\text{H}_{18}(\text{CH}_2) \cdot \text{COOH}$, is formed when santonin is heated with hydriodic acid and amorphous phosphorus; it crystallises from dilute alcohol in delicate needles, melts at 174° , and is readily soluble in ether, alcohol, and benzene. The *silver* salt is a white, amorphous precipitate, which is reduced on boiling with water. Cannizzaro and Cernelutti obtained an acid (m. p. $178-179^\circ$) in the above given manner, to which they erroneously ascribed the formula $\text{C}_{15}\text{H}_{20}\text{O}_3$, this acid being, doubtless, identical with that just described.

When santonin is dissolved in a mixture of glacial acetic acid and alcohol, and an excess of zinc-dust gradually added to the hot solution, a *dilactone*, $\text{C}_{30}\text{H}_{36}\text{O}_4$, separates from the filtrate on adding water, whilst a compound resembling santonin, but melting at $163-164^\circ$, is isolated on evaporating the mother liquor. The dilactone crystallises from alcohol in yellowish-green needles, melts at $200-201^\circ$, and when dissolved in alcoholic alkali, the solution evaporated, and the residue redissolved in water and hydrochloric acid added, an isomeride more sparingly soluble in alcohol and crystallising therefrom in small, white needles is obtained; this melts at $260-261^\circ$ forming a dark liquid. The compounds are provisionally distinguished as α - and β -santogenenic dilactone.

A. R. L.

Santonin. By J. KLEIN (*Ber.*, **25**, 3317—3318).—When bromine and santonin are dissolved in molecular proportion in glacial acetic acid, and the solution, after remaining for some hours, is poured into water, an additive compound, $\text{C}_{15}\text{H}_{18}\text{O}_3 \cdot \text{C}_2\text{H}_4\text{O}_2 \cdot \text{Br}_2$, is precipitated; when crystallised from alcohol, it melts a little above 60° , decomposes on exposure to light, but is stable when kept in the dark. Santonin is regenerated when the additive compound is boiled with aqueous alcoholic potash; whilst *bromosantonin*, $\text{C}_{15}\text{H}_{17}\text{BrO}_3$, is obtained when it is boiled with alcohol. The latter crystallises from alcohol in leaflets, melts at $149-151^\circ$, and its behaviour towards nitric acid indicates that the bromine is contained in the aromatic nucleus. Santonin, when dissolved in alcohol or ether and treated with hydrogen chloride, does not form an additive compound, but when treated with phosphoric chloride (2 mols.), it yields a *chloride*, $\text{C}_{15}\text{H}_{16}\text{Cl}_2\text{O}$, which seems by its behaviour towards nitric acid to contain the chlorine in the side-chain.

A. R. L.

Cephalanthin. By C. MOHRBERG (*Chem. Centr.*, 1892, ii, 363; from *Arb. Pharm. Inst. Dorpat*, **8**, 20—50; compare Claasen, *Abstr.*, 1890, 171).—By extracting cephalanthus bark with boiling water and fractionally precipitating the extract with lead acetate, in three fractions, there were obtained in the first cephalanthin and colouring matters, in the second a tannin, and in the third a saponin. But the greater portion of the cephalanthin is contained in the pressed bark, and is obtained by boiling this with lime water, precipitating the lime with carbonic anhydride, and, finally, the cephalanthin with hydrochloric acid. It is very bitter, even in dilution of 1 : 15,000,

very soluble in alcohol, ethyl acetate, ammonia, and soda, slightly in hot and cold water, ether, and chloroform, not at all in benzene and light petroleum. It is a feeble acid, and displaces carbonic anhydride from carbonates. Its composition is $C_{22}H_{34}O_6$; it begins to liquefy at 177° , and melts at 180.1° (corr.), and in alkaline solution has $[\alpha]_D = 20.25^\circ$. Strong sulphuric acid colours it orange, hydrochloric acid violet, sulphovanadic acid pink, dilute gallic acid or strong sulphuric at 70° at first red, then violet, α -naphtholsulphonic and thymolsulphonic acids violet or reddish-violet. Acids decompose it into a sugar, $C_6H_{12}O_6$ (whose phenylosazone melts at 196 — 198°), and an acid substance, *cephalantein*, $C_{16}H_{23}O_3$; it is thus a glucoside.

The cephalanthus tannin mentioned above is a reddish-yellow powder, soluble in alcohol and hot water, and gives a green coloration with ferric salts. It is probably a mixture of "true tannic acid" with another substance, the cephaletin of Claasen. The cephalanthus saponin is a poison which dissolves the blood corpuscles; it is not very active, however.

Cephalanthin, when injected, acts as a poison, dissolving the blood corpuscles, the colouring matter of which goes into the serum and the urine as oxyhæmoglobin, and is then changed into methæmoglobin. Cramp, vomiting, and paralysis appear, and jaundice, caused by an enormously increased secretion of bile. Among the earlier symptoms are movements of the intestines, but neither the heart, vagus nerve, nor vasomotor system is affected. The iron separated out in the liver gets into the spleen, lymphatic glands, and marrow, and is used up in the formation of blood; a part goes into the kidneys.

C. F. B.

Identity of Cascarin and Rhamnoxanthin. By T. L. PHIPSON (*Compt. rend.*, 115, 474).—The cascarin obtained by Leprince (Abstr., 1892, 1483) from *Cascara sagrada* (*Rhamnus prushiana*) is identical with the rhamnoxanthin obtained by the author in 1858 from the bark of *Rhamnus frangula*.

C. H. B.

Action of Hydrogen Peroxide on Piperidine Bases. By G. MERLING (*Ber.*, 25, 3123—3127).—Hydroxy-bases are obtained from tropidine, tropine, hydrotropidine, and methyl- α - and - β -pipercoline by allowing these compounds to remain with 15 parts of commercial hydrogen peroxide at the ordinary temperature for some days. The hydroxy-bases are colourless, crystalline compounds, are very hygroscopic, cannot be distilled without decomposition, and have a faint alkaline reaction. They are unaltered when heated with concentrated hydrochloric acid at 140 — 170° . The action of hydrochloric acid on hydroxytropine has not been examined. Hydroxyhydrotropidine, $C_8NH_{15}O$, obtained from hydrotropidine, is not identical with tropine or with Liebermann's pseudotropine, and therefore the author concludes that the oxygen atom is not attached to a β - or γ -methylene group. The author believes that these hydroxymethylpiperidine bases contain the complex $HO \cdot CH_2 \cdot N <$, since they do not lose water when heated with concentrated hydrochloric acid, and secondary piperidine bases are not hydroxylated when treated with hydrogen peroxide. Hydr-

oxytropidine and hydroxymethylpiperidine, when warmed with concentrated hydriodic acid and then treated with sulphurous acid yield tropidine and methylpiperidine respectively.

α -Methyltropidine, C_9NH_{15} , is converted by hydrogen peroxide into the compound $C_9NH_{15}O$. The latter is very unstable, and decomposes when warmed in aqueous solution, probably yielding dihydrobenzaldehyde and dimethylamine.

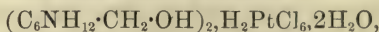
The above hydroxy-bases were characterised by means of the platinochlorides.

Hydroxytropidine platinochloride, $(C_7NH_{10} \cdot CH_2 \cdot OH)_2 \cdot H_2PtCl_6$, crystallises from water in large, lustrous, orange-yellow plates, melts at 220° with decomposition, and is sparingly soluble.

Hydroxytropine platinochloride, $(C_7NH_{12}O \cdot CH_2 \cdot OH)_2 \cdot H_2PtCl_6 \cdot 2H_2O$, crystallises in orange-yellow tablets, is easily soluble, and effloresces on exposure to air.

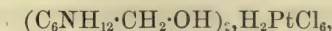
Hydroxyhydrotropidine platinochloride, $(C_7NH_{12} \cdot CH_2 \cdot OH)_2 \cdot H_2PtCl_6$, crystallises in lustrous, orange-yellow prisms, melts at 228° with decomposition, and is easily soluble.

Hydroxymethyl- α -pipecoline platinochloride,



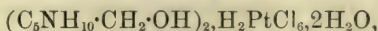
crystallises from hot water in orange crystals, when dry melts at 202° with decomposition, and is very sparingly soluble in cold water.

Hydroxymethyl- β -pipecoline platinochloride,



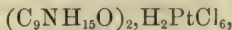
crystallises in orange-red prisms, melts at $196-197^\circ$ with decomposition, and is easily soluble.

Hydroxymethylpiperidine platinochloride,



crystallises in beautiful, orange-red prisms, when dry it melts at 194° with decomposition, and is sparingly soluble.

Hydroxydihydrobenzyltrimethylamine platinochloride,



is obtained in yellow leaflets which are sparingly soluble, and blacken when heated with water.

E. C. R.

Non-nitrogenous Acids derived from Pyridinecarboxylic acids. By H. WEIDEL and J. HOFF (*Monatsh.*, 13, 578—602; compare Abstr., 1891, 733, 1525).—Cinchonic acid, which, as has been previously shown, is formed by the action of sodium amalgam on cinchomeronic acid, $C_7H_5NO_4$, behaves generally in the same way as a bibasic acid, and, on saturation with carbonates, yields secondary salts, of the formula $C_7H_5M_2O_6$, which, however, are converted by hydroxides into tertiary salts, $C_7H_7M_3O_7$. On ethylation, cinchonic acid gives a compound containing two ethyl groups, $C_7H_5O_6Et_2$, and this is converted by phosphorus pentachloride into an unstable chloro-compound, which, on treatment with alcohol, yields the triethyl salt of the tricarboxylic acid, $C_4H_7Cl(COOH)_3$.

On reduction with hydriodic acid, cinchonic acid forms the tri-carboxylic acid, $C_7H_{10}O_6$, which was obtained by the authors in the form of two stereo-isomeric modifications. When this acid is heated, carbonic anhydride escapes, and α -methylglutaric acid is formed.

On dry distillation, cinchonic acid loses water and carbonic anhydride, and forms pyrocinchonic anhydride, $C_6H_6O_2$, which readily combines with nascent hydrogen, and is converted thereby into dimethylsuccinic acid. When digested with sodium ethoxide, cinchonic acid forms δ -hydroxyethylsuccinic acid, which, on reduction, yields ethylsuccinic acid. The behaviour of cinchonic acid characterises it as a lactonic acid, and points to its being δ -hydroxy- $\alpha\beta\gamma$ -butenyl-tricarboxylic acid; moreover, the decomposition with nascent hydrogen from sodium amalgam takes place in a manner perfectly analogous to that observed in the reduction of pyridinecarboxylic acid, in which case the formation of the CO group in the α -position is also observed.

G. T. M.

Some Ammonium Compounds. By H. DECKER (*Ber.*, 25, 3326—3328).—The formation of quinolone derivatives (*Abstr.*, 1892, 729) proceeds without the addition of potassium ferrieyanide when concentrated solutions of quinoline alkyl iodides are distilled with steam in the presence of alkali; the quinolones are dissolved in the aqueous distillate, but an oil, consisting of alkyl-dihydroquinoline, also passes over. The author considers it not improbable that an

ammonium hydroxide, $\begin{array}{c} \text{CH}\cdot\text{C}_6\text{H}_4 \\ || \\ \text{CH}-\text{CH} \end{array} \gg \text{NR}\cdot\text{OH}$, is initially formed, which

changes into a hydroxydihydroquinoline, $\begin{array}{c} \text{CH}-\text{C}_6\text{H}_4 \\ || \\ \text{CH}\cdot\text{CH}(\text{OH}) \end{array} \gg \text{NR}$, and then decomposes into the above-mentioned oxidation and reduction products.

A. R. L.

Bases from Polei Oil. By O. WALLACH (*Annalen*, 272, 122—125; compare Beckmann and Pleissner, *Abstr.*, 1891, 936).—Two bases are formed when oil of polei, from *Mentha pulegium*, is heated with ammonium formate. The one boils below 170° , and its salts are readily soluble; its *hydrochloride*, $C_7H_{15}N\cdot HCl$, melts at 174 — 176° , and distils at a higher temperature without appreciable decomposition; its *platinochloride*, $(C_7H_{15}N)_2\cdot H_2PtCl_6$, separates from hot water in crystals.

The other base boils at about 250° , and its salts are comparatively sparingly soluble; its *hydrochloride* crystallises well, and has the composition $C_{14}H_{27}N\cdot HCl$ or $C_{15}H_{29}N\cdot HCl$; its *nitrate* is almost insoluble in cold water; its *platinochloride* is crystalline but unstable.

When the liquid pulegone oxime is reduced with sodium and alcohol, it is converted into a base which is quite different from either of the two compounds mentioned above, but which has certain points of similarity with fenchylamine and menthylamine; the crystalline pulegone oxime shows quite a different behaviour.

F. S. K.

Quinine Double Salts. By E. GRIMAUX (*Compt. rend.*, 115, 608—610).—The author has previously adduced evidence in support

of the view that, in basic quinine salts, the acid is not united to the nitrogen of the quinoline group, but to another group, probably of the character of piperidine. If this hypothesis is correct, the quinoline group should be able to unite with another acid and produce double salts.

When 30 parts of crystallised basic quinine sulphate (1 mol.) is dissolved in 24.9 c.c. of hydrochloric acid of the sp. gr. 1.050 (2 mols.), and the solution is allowed to evaporate spontaneously in dry air, the salt, $(C_{20}H_{22}N_2O_2)_2 \cdot 2HCl \cdot H_2SO_4 + 3H_2O$, is obtained in acicular crystals, which lose 3 mols. H_2O at 100° . One part of the anhydrous salt dissolves in 1.16 parts of water at 25° . The hydrated salt melts at 120° , and the anhydrous salt melts, indistinctly, with some decomposition, at 165 – 170° . If only half the quantity of hydrochloric acid is used, solution takes place much less easily, and the hot liquid, when cooled, deposits basic quinine sulphate. On further evaporation, it yields the hydrochlorosulphate.

Quinine hydrobromosulphate, $(C_{20}H_{22}N_2O_2)_2 \cdot 2HBr \cdot H_2SO_4 + 3H_2O$, is obtained in a similar manner, by dissolving the basic sulphate (1 mol.) in hydrobromic acid (2 mols.). It forms a hard, white mass of small needles, loses 3 mols. H_2O at 100° , and is less soluble than the chlorine compound.

The hydriodosulphate is obtained in a similar manner, and forms yellowish crystals, which lose water in a dry vacuum or at 100° , and become brown, but absorb water and regain their yellow colour when exposed to the air.

Phosphoric acid yields analogous double salts. The chlorine compound has the composition $(C_{20}H_{22}N_2O_2)_2 \cdot 2HCl \cdot H_3PO_4 + 9H_2O$. They all crystallise in needles, the bromide with 7 mols. H_2O , and the iodide with 6 mols. H_2O . C. H. B.

Hydrastine. By M. FREUND (*Annalen*, **271**, 311–408).—In this paper, the author gives, in a connected manner, the results of the investigations by which the constitution of hydrastine has been determined, and also briefly describes the more important decomposition products of the alkaloid; most of the work has already been published (compare Abstr., 1890, 53, 534; 1891, 92, 93, 1578), but the following results are communicated for the first time:—Two isomerides of the composition $C_{10}H_9NO_4$ are produced when hydrastine is oxidised with potassium permanganate at about 40° (compare Abstr., 1889, 627 and 1220); the two compounds are more easily prepared by heating hydrastinic acid, $C_{11}H_9NO_6$, at 170° for a few minutes, and are separated with the aid of boiling alcohol. The one is deposited from the hot alcoholic extract in yellowish crystals, melts at 211 – 212° , and is readily soluble in hot water, alcohol, and glacial acetic acid, but insoluble in benzene, ether, carbon bisulphide, and chloroform; it can also be obtained by heating methylamine hydrastinate at 180° . The isomeride is insoluble in boiling alcohol, benzene, and chloroform, and only sparingly in water and glacial acetic acid; it separates from concentrated hydrochloric acid in crystals, melts at 280° , and, like the compound just described, dissolves in concentrated sulphuric acid with a blue coloration.

Hydrastic acid methylimide, $C_{10}H_7NO_4$, prepared by boiling hydrastinic acid with dilute nitric acid, melts at $227-228^\circ$, not at 233° as previously stated (Abstr., 1889, 1220).

Hydrastic acid, $C_9H_6O_6$, crystallises from hot water in lustrous, hexagonal prisms, or in long, broad needles, and is almost insoluble in chloroform and light petroleum, and only very sparingly soluble in toluene, but more readily in ether, acetone, and ethyl acetate, and very readily in alcohol; when very slowly heated, it sinters at $171-172^\circ$ and melts at $173.5-174^\circ$ with effervescence, but when very quickly heated, the temperature can be raised to $185-187^\circ$ before the acid melts and passes into the anhydride (see below). The *barium* salt, $C_9H_4O_6Ba + H_2O$, separates from hot water in plates. The *silver* salt, $C_9H_4O_6Ag_2$, is a colourless compound, almost insoluble in water; the *silver hydrogen* salt, $C_9H_5O_6Ag$, prepared from the ammonium hydrogen salt, crystallises in microscopic needles, and is sparingly soluble in hot water. The *copper* salt, $C_9H_4O_6Cu$, crystallises in small, dark green plates or prisms; the *copper hydrogen* salt, $(C_9H_5O_6)_2Cu + 6H_2O$, crystallises in light blue needles. The *ammonium hydrogen* salt, $C_9H_5O_6 \cdot NH_4$, crystallises from hot water in lustrous needles, sinters at $209-212^\circ$, and melts at $245-250^\circ$ with decomposition. The methylamine salt, $C_9H_6O_6 \cdot NH_2Me$, is formed when hydrastic acid methylimide is boiled with 33 per cent. potash until the solution begins to become turbid (compare Abstr., 1889, 1220); it crystallises from hot water, melts at $225-226^\circ$, and is practically insoluble in most organic solvents. The *dimethyl* salt, $C_9H_4O_6Me_2$, prepared by passing hydrogen chloride into a methyl alcoholic solution of the acid, crystallises from alcohol in colourless plates, and melts at $88-89^\circ$; the *methyl hydrogen* salt, $C_9H_5O_6Me$, melts at 136° , and is soluble in hot water, ether, and alcohol. The *anhydride*, $C_9H_4O_6$, crystallises from alcohol in needles, melts at 175° , and is only sparingly soluble in alcohol; it gives the fluorescein reaction.

Hydrastimide, $C_9H_5O_4N$, is formed when the ammonium hydrogen salt is heated for some time at its melting point; it crystallises from glacial acetic acid in colourless, iridescent plates, sinters at 270° , melts at $275-277^\circ$, and is moderately easily soluble in acetone, but more sparingly in chloroform and water; its solutions show a slight fluorescence.

Dichlorhydrastic chloride, $CCl_2 < \overset{O}{\text{O}} > C_6H_2(COCl)_2$, is formed when hydrastic acid is heated at $175-185^\circ$ with phosphorus pentachloride; it is an oil, and is gradually decomposed by water, being converted into a crystalline compound, which melts at $142-144^\circ$, and is, doubtless, *dichlorhydrastic acid*.

Normetahemipinic acid, $C_8H_6O_6 + H_2O$, is obtained when dichlorhydrastic acid is heated with water; it sinters at 190° and melts at 248° , being converted into the anhydride; it is identical with the acid described by Rossin (Abstr., 1892, 180), as is proved by crystallographic measurements and by the properties of its anhydride and ethyl hydrogen salt.

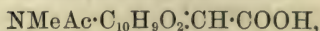
Benzoylhydrastinine, $C_{11}H_{12}NO_3Bz$, prepared by shaking hydrastinine

with soda and benzoic chloride, crystallises from dilute alcohol, and melts at 98—99°; its *oxime*, $C_{11}H_{12}NO_2Bz \cdot NOH$, melts at 146°.

Benzoylhydroxyhydrastinine hydrate, $C_{11}H_{12}NO_4Bz + H_2O$, is formed when benzoylhydrastinine is oxidised with potassium permanganate in presence of alkali; it crystallises from dilute alcohol in prisms, loses its water at 105°, melts at 169—170°, and dissolves freely in alkalis.

Acetylhydrastinine, $C_{11}H_{12}NO_3Ac$, is obtained when hydrastinine is warmed with acetic anhydride in benzene solution; it crystallises from hot water in concentrically grouped needles, melts at 105°, and forms a crystalline hydrochloride which is decomposed by water.

Acetylmethylamidohydrastyleneacetic acid,



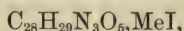
is formed when hydrastinine is boiled with acetic anhydride for two hours; it separates from hot acetic acid in crystals, melts at 219°, and is almost insoluble in cold water and ether, but soluble in alcohol, benzene, and chloroform. The compound obtained by treating hydrastinine with propionic anhydride in like manner melts at 135°. The *bromo-derivative*, $C_{15}H_{16}BrNO_5$, prepared by treating acetylmethylamidohydrastyleneacetic acid with bromine in chloroform solution, crystallises from hot dilute alcohol in colourless needles, and melts at 180—181°. The *barium salt*, $(C_{15}H_{16}NO_5)_2Ba$, is crystalline. The *methyl salt*, $C_{15}H_{16}NO_5Me$, crystallises from hot water in needles, and melts at 147°.

Phenylmethylhydrastylthiocarbamide, $C_{18}H_{18}N_2O_3S$, is obtained when hydrastinine is treated with phenylthiocarbimide in alcoholic solution; it separates from alcohol in almost colourless needles melting at 126°.

Methylhydrasteineoxime anhydride, $C_{22}H_{24}N_2O_6$, can be prepared by boiling methylhydrasteine with hydroxylamine hydrochloride in moderately concentrated aqueous solution; it crystallises from alcohol in lustrous, hexagonal plates, containing 1 mol. C_2H_6O , which is expelled at 80—85°; it melts at 158° and is almost insoluble in water and cold alcohol, but readily in hot alcohol. The *hydrochloride*, $C_{22}H_{24}N_2O_6 \cdot HCl + 3H_2O$, prepared by adding hydrochloric acid to an alcoholic solution of the base, crystallises from water in small, quadratic plates, and melts at 221°; the anhydrous salt is obtained in microscopic crystals when hydrogen chloride is passed into an alcoholic solution of the base. The *nitrate*, $C_{22}H_{24}N_2O_6 \cdot HNO_3$, crystallises from boiling alcohol in small prisms. The *sulphate*, $C_{22}H_{24}N_2O_6 \cdot H_2SO_4 + C_2H_6O$, crystallises from alcohol in lustrous, hexagonal plates, sinters at 80°, melts at 90°, and begins to decompose at 110°. The *methiodide*, $C_{22}H_{24}N_2O_6 \cdot MeI + 2H_2O$, crystallises from water in compact, yellowish prisms, loses its water at 125—130°, and melts at 155—156°; when boiled with potash, it is decomposed with evolution of trimethylamine, yielding a compound which crystallises from alcohol in yellow, hexagonal prisms, melts at 184—185°, and has the composition $C_{20}H_{17}NO_6$.

Methylhydrasteinephenylhydrazone anhydride, $C_{28}H_{29}N_3O_5$, is formed when methylhydrasteine is boiled with an alcoholic solution of

phenylhydrazine hydrochloride; it crystallises from alcohol in yellowish, quadratic prisms, melts at 175—176°, and is insoluble in water and only sparingly soluble in boiling alcohol. The *hydrochloride*, $C_{28}H_{29}N_3O_5, HCl$, crystallises in slender needles, and melts at 220—222°. The *nitrate*, $C_{28}H_{29}N_3O_6, HNO_3$, melts at 203—204°, and separates from hot alcohol in crystals. The *methiodide*,



is a transparent, highly-refractive, crystalline compound melting at 243°, and moderately easily soluble in hot dilute alcohol; when boiled with concentrated potash, it is decomposed with evolution of methylamine, being converted into a pale yellow, crystalline compound, which melts at 162—164°, and has the composition $C_{26}H_{22}N_2O_5$.

Nitromethylhydrastimide, $C_{22}H_{23}N_3O_7$, is obtained, together with dihydroxymethylhydrastimide, hemipinimide, and other compounds, when methylhydrastimide (compare Freund and Heim, Abstr., 1891, 92) is warmed with a mixture of equal parts of nitric acid of sp. gr. 1.15 and water, until the methylhydrastimide nitrate, which separates from the solution at first, has redissolved; the solution is then immediately cooled. The nitro-compound separates from hot alcohol in lustrous, red crystals, which contain 1 mol. C_2H_6O ; these crystals sinter at about 85°, melt at about 95°, and then solidify, melting again at 138° to a dark red liquid which is completely decomposed at 170°; it also crystallises with benzene and with chloroform. Its salts crystallise well, and, with the exception of the nitrate, are all readily soluble in boiling alcohol and in hot water. The *hydrochloride*, $C_{22}H_{23}N_3O_7, HCl$, prepared by passing hydrogen chloride into a hot alcoholic solution of the base, crystallises in lustrous, yellow needles, and melts at 202—203°. The *nitrate*, $C_{22}H_{23}N_3O_7, HNO_3$, separates from dilute alcohol in crystals melting at 212°. The *sulphate*, $(C_{22}H_{23}N_3O_7)_2, H_2SO_4$, crystallises in yellow, microscopic needles, and melts at 195—196°; the *acid sulphate*, $C_{22}H_{23}N_3O_7, H_2SO_4$, forms golden needles, and melts at 250°. The *methiodide*, $C_{22}H_{23}N_3O_7, MeI$, crystallises from hot alcohol in orange plates, and decomposes at about 250°, but without melting.

Dihydroxymethylhydrastimide, $C_{22}H_{24}N_2O_7$, crystallises from hot alcohol in colourless needles, melts at 151°, and is soluble in acids and alkalis; when heated with dilute nitric acid, it is converted into hemipinimide. The *platinochloride*, $(C_{22}H_{24}N_2O_7)_2, H_2PtCl_6$, crystallises from hot dilute alcohol in needles, and melts at 203—205°. The *methiodide*, $C_{22}H_{24}N_2O_7, MeI$, crystallises from water in colourless prisms, and melts at 190°. F. S. K.

Cytisine and Ulexine. By A. PARTHEIL (*Arch. Pharm.*, 230, 448—498).—The author has already stated (Abstr., 1891, 231 and 750) that cytisine from laburnum and other varieties of *Cytisus* is identical with Gerrard's ulexine from *Ulex europæus*, and that it has the formula $C_{11}H_{14}N_2O$. For the preparation of the alkaloïd from either source, the pulverised seeds are extracted in a percolator with 60 per cent. alcohol acidified with acetic acid; chloroform is to be recom-

mended for extracting the free base, but its application, in the manner described by Buchka and Magalhaes (Abstr., 1891, 587), is not desirable, as an emulsion is formed. Gerrard and Symon state that a second base is present along with ulexine in the seeds of *Ulex europæus*, but the author failed to recognise it; he has, however, separated choline from the seeds of the *Cytisus* species.

Small quantities of cytisine base may be freed from the accompanying colouring matters by crystallisation from boiling light petroleum; the pure base crystallises from absolute alcohol in large, colourless, anhydrous prisms which are not deliquescent, melts at 152–153°, and is readily soluble in water, alcohol, and chloroform, less so in benzene and amyl alcohol, almost insoluble in cold light petroleum, and insoluble in pure ether. Its specific rotatory power in aqueous solution is $[\alpha]_{D17^\circ} = -119.57$, and analysis confirmed the formula given above. For the detection of the alkaloid, Magalhaes' reaction serves; this consists in adding thymol to a solution of cytisine in concentrated sulphuric acid and heating, when a yellow coloration, finally passing into an intense red, is produced.

The author next describes a number of derivatives of cytisine, most of which are already known, and compares them with the corresponding derivatives of ulexine, thereby proving the identity of the two alkaloids. Among these are the nitrate, $C_{11}H_{14}N_2O.HNO_3 + H_2O$, which has a specific rotatory power in aqueous solution $[\alpha]_{D17^\circ} = -82.4$, the two platinochlorides, $(C_{11}H_{14}N_2O)_2.H_2PtCl_6$ and $C_{11}H_{14}N_2O.H_2PtCl_6 + 2\frac{1}{2}H_2O$, the aurochloride melting at 212–213°, the acetyl derivative melting at 208°, and the methiodide which melts at 270° (compare Buchka and Magalhaes. Abstr., 1891, 587 and 750). Methylcytisine melts at 134°; the platinochloride crystallises with $2\frac{1}{2}$ mols. H_2O , and the aurochloride melts at 196° (*loc. cit.*). Ethylcytisine is a yellow liquid, and yields a platinochloride which crystallises with 1 mol. H_2O . Magalhaes' dimethylcytisine forms a platinochloride crystallising with $2\frac{1}{2}$ mols. H_2O , and gives rise to dimethylcytisine methiodide when heated on the water-bath with methyl iodide; the methiodide decomposes on boiling with concentrated aqueous potassium hydroxide with the evolution of trimethylamine, whilst chloroform extracts from the cold solution a base giving an amorphous, yellow platinochloride, $(C_{10}H_{13}NO_2)_2.H_2PtCl_6$. On distilling cytisine with soda lime, a base, $C_9H_{13}N$, probably a pyridine derivative, is obtained; this is, perhaps, related to the base $C_{10}H_{13}NO_2$, just mentioned. The alkaloid gives no evidence of the presence of the group CO, in that it does not react with phenylhydrazine.

The precise constitution of cytisine is still obscure, but its behaviour towards methyl iodide, acetic anhydride, and nitrous acid (*loc. cit.*) shows that one of its nitrogen atoms is in secondary combination; the second nitrogen atom is either in tertiary or quaternary combination. That the oxygen atom exists neither in the form of methoxyl nor hydroxyl is proved by the fact that methylcytisine does not yield an acetyl derivative. The research is being continued.

A. R. L.

Organic Chemistry.

Action of Stannic Chloride on Halogen Derivatives of Methane. By G. GUSTAVSON (*J. Russ. Chem. Soc.*, **23**, 253—258).—When stannic chloride (1 mol.) is heated with carbon tetrabromide (1 mol.) at the temperature of boiling aniline (184°) for an hour, 26.16 per cent. of the chlorine in the chloride is replaced by bromine. Under similar conditions, only 0.7 per cent. of the halogens are interchanged when stannic chloride and bromoform are heated together in such proportions that the halogens in the two substances are equivalent.

The action in the case of methylene bromide is also slight, 1.05 per cent. of the halogens changing places.

When the mixtures of the chloride with bromoform and with methylene bromide are heated for 150 hours at 130—135°, the interchange takes place to the extent of 1.92 per cent. and 2.89 per cent. respectively. Titanium tetrachloride acts like stannic chloride; with bromoform, 3.54 per cent. of the chlorine is replaced after heating for 150 hours at 135°.

The following numbers were obtained with the iodine substitution products of methane after standing in the dark with stannic chloride for seven years:—Iodoform, no action; methylene iodide, 1.2 per cent.; methyl iodide, 34 per cent. J. W.

Preparation of Pure Chloroform from Salicylide Chloroform. By R. ANSCHÜTZ (*Ber.*, **25**, 3512—3513).—The author proposes to employ the compounds formed by salicylide and orthohomosalicylide with chloroform (this vol., i, 165) for the preparation of the latter substance in the pure state. These compounds, which contain about one-third of their weight of chloroform, are formed by simply boiling salicylide or orthohomosalicylide with chloroform for a few minutes; they can be preserved for any length of time in closed vessels without undergoing change, and readily give off chloroform on warming. The chloroform thus obtained remains unaltered on keeping, whereas the ordinary chloroform always becomes contaminated with carbonyl chloride. H. G. C.

Preparation of Silver Acetylde from Acetylenedicarboxylic acid. By W. LOSSEN (*Annalen*, **272**, 139—141).—Silver acetylde can be very easily prepared by gradually adding the theoretical quantity of a hot 10 per cent. solution of silver nitrate to a hot solution of sodium acetylenedicarboxylate; each addition of the silver solution produces a vigorous effervescence, due to the escape of carbonic anhydride, and the theoretical quantity of silver acetylde is obtained as a dirty yellow precipitate. F. S. K.

Action of Hydrogen Chloride and Hydrogen Bromide on Liquid α -Dichlorethyl Cyanide. By J. TROEGER (*J. pr. Chem.* [2], **46**, 353—380; compare *Abstr.*, 1887, 1024).—When dry hydrogen

chloride is passed into liquid α -dichlorethyl cyanide, the sides of the flask become covered with crystals; the ultimate analysis of this substance, and determinations of its molecular weight by the cryoscopic method, indicate that it is *dimolecular α -dichlorethyl cyanide*, $(\text{CMeCl}_2\text{CN})_2$. The new compound forms colourless, lustrous, monosymmetric crystals (measurements given), and begins to decompose at 130° without previous melting; it dissolves easily in cold methyl alcohol and molten phenol, but is insoluble in other organic solvents. When heated with sulphuric acid (1 : 1), it yields dichloropropionic acid (compare Otto and Voigt, *Abstr.*, 1887, 1024). When shaken with water at the ordinary temperature, it partially dissolves, and crystals almost immediately begin to separate from the solution, which acquires a strongly acid reaction; the crystals dissolve readily in organic solvents, but cannot be purified by recrystallisation, inasmuch as no sharper melting point than $75\text{--}79^\circ$ can be thus obtained; by dissolution in sodium hydroxide and reprecipitation with hydrochloric acid, the crystals can be obtained of constant melting point, $82\text{--}83^\circ$. The ultimate analysis and molecular weight determination of this substance show that it is *α -dichloropropionylhydroxyethyl cyanide*, $\text{CMeCl}_2\cdot\text{CO}\cdot\text{CMe}(\text{CN})\cdot\text{OH}$; when it, or the dimolecular α -dichlorethyl cyanide, is heated with water, it is converted into α -dichloropropionamide (m. p. 114° , generally given as 116°).

Another new compound, $\text{C}_6\text{H}_5\text{Cl}_3\text{N}_2$, is obtained in lustrous, prismatic needles, which melt at 48° , and dissolve in most solvents, when dimolecular α -dichlorethyl cyanide is treated with alcoholic ammonia; it has not been further investigated. When the cyanide is suspended in light petroleum, and subjected to the action of dry ammonia, a yellowish-brown oil is obtained; the analyses of this gave ill-defined results, but from the fact that two molecular proportions of ammonium chloride are eliminated, the author concludes that its formula is $\text{C}_6\text{H}_4\text{Cl}_2\text{N}_2$, and is confirmed in this opinion by the fact that it is converted into a chloracrylic acid by the action of sulphuric acid; the oil is volatile with steam, and the distillate partially solidifies, the solid portion having a poppy-like odour.

The action of hydrogen bromide on liquid α -dichlorethyl cyanide produces a compound, $\text{C}_6\text{H}_6\text{Cl}_2\text{Br}_2\text{N}_2$, which is very similar in all respects to dimolecular dichlorethyl cyanide; it has no definite melting point. It dissolves in methyl alcohol and molten phenol; from its solution in the former, it cannot be precipitated by ether, in which respect it differs from the chloro-derivative. The product of its decomposition with water melts at about 73° , and has a chlorine content corresponding with α -dichloropropionylhydroxyethyl cyanide (see above). During the action of the hydrogen bromide, a by-product, $\text{C}_3\text{H}_7\text{Cl}_2\text{BrN}_2$ (?), which crystallises in large, slender, white, tabular prisms, and melts at $147\text{--}148^\circ$, is formed; by the action of aqueous ammonia, it yields α -dichloropropionamide. A. G. B.

Reactions of Ferric Salts with Thiocyanates. By H. M. VERNON (*Chem. News*, 66, 177—179, 191—193, 202—203, 214—215). —In these investigations, colorimetric observations were adopted for

comparison, and were made in vertical, flat-bottomed tubes, by comparing the solution to be tested with an adjustable column, either of a 0.1 per cent. solution of picocarmine, or, in some cases, of a dilute solution of ferric thiocyanate, prepared from lithium thiocyanate and excess of ferric chloride. Solutions were examined containing 1, 2, 4, 7, 11, 18, 30, and 100 equivalents of ferric chloride to 1 part of potassium thiocyanate, and diluted to various degrees, ranging from 2- to 120-fold. In equivalent quantities, these two reagents react almost completely at infinite concentration, to form ferric thiocyanate; but solutions less dilute than those mentioned above were too deep in colour, whilst solutions containing one or two equivalents of ferric chloride, when diluted above 40 times, were too weak in tint for colorimetric examination. The decrease in ferric thiocyanate coloration, resulting from the dilution of the solutions from 8- to 120-fold, in the strongest solution, was 27 per cent., in the 30 : 1 solution over 60 per cent., in the 18 : 1 solution 73 per cent., whilst diluting from 2- to 32-fold in the case of the 1 : 1 solution resulted in a reduction of the coloration, amounting to 94 per cent.; the stability of the ferric thiocyanate, therefore, appears to vary regularly with the amount of ferric chloride present; moreover, the amount of ferric thiocyanate formed in these solutions varies with the dilution in accordance with the law of mass. The action of ferric chloride is twofold; in most cases it forms a solution in which the ferric thiocyanate is more stable than in pure water, but in very strong solutions, it exerts a decolorising and presumably a destructive action on the deep-coloured thiocyanate.

The examination of a similar set of solutions, in which the proportion of ferric chloride was kept constant, and that of the potassium thiocyanate varied, indicated that, although the ferric thiocyanate was more stable in a solution of potassium thiocyanate than in water, yet the decrease in colour on dilution did not, in this case, follow the law of mass, probably owing to the presence of impurities.

Numerous other experiments with various ferric salts and thiocyanates led to the following conclusions:—That the colour reactions of ferric chloride, nitrate, sulphate, tartrate, citrate, and acetate with potassium, ammonium, sodium, lithium, calcium, and barium thiocyanates, indicate that the formation of ferric thiocyanate in these cases is dependent on two factors, one being the nature of the acid of the ferric salt, the other the nature of the base of the thiocyanate; the former exerting an action somewhat in accord with the relative affinities of the acids, whilst the latter shows no such relationship. In all these cases, except with the acetate, the colour of the ferric salt caused no inconvenience.

Heating the solutions increases the activity of the various reactions, and when those that favour the formation of ferric thiocyanate predominate, an increase of colour is observed, and *vice versa*. Therefore, by heating at 20°, 30°, 40°, 50°, and 60°, or when decomposition ensued at some intermediate temperature, an increase of colour is observed with thiocyanates and ferric salts of monobasic acids, and a decrease with ferric salts of polybasic acids.

D. A. L.

Acid of Zinc Ethide on Acid Chlorides. By A. GRIGOROVITCH and D. PAVLOFF (*J. Russ. Chem. Soc.*, **23**, 159—178).—Isobutyric chloride (1 mol.) and zinc ethide (2 mols.) were brought together in a flask at a low temperature and allowed to remain for three days at 0°, the temperature being subsequently raised to about 18°. After a week, ethylene began to be evolved from the mixture, the evolution continuing for a long time; on the expiry of 30—35 days, the contents of the flask began to thicken, and after 65 days, had become gelatinous. Three months later, the products of the reaction were treated with ice and water, when an oily layer separated, having a caustic taste and the odour of camphor; this was distilled with steam, separated by means of potash, carefully dried, and fractionated. On continued fractionation, it separated into four portions boiling at 77—79°, 114—115·5°, 126—127°, and 158—161° respectively. The liquid boiling at 77—79° was proved to be ethyl alcohol, and that boiling at 114—115° was a ketone of the composition $C_6H_{12}O$; as the latter yielded acetone, isobutyric acid, and formic acid on oxidation with chromic mixture, it was ethyl isopropyl ketone.

Ethylisopropylcarbinol.—This was the chief constituent of the fraction which boiled at 126—127°. It is a colourless liquid with a pleasant ethereal odour resembling that of peppermint and a somewhat caustic taste, it boils at 127—127·5° under a pressure of 721 mm., and becomes viscid in a mixture of ice and salt. Its sp. gr. at 0°/0° is 0·8383, and at 20°/20° 0·8243, the mean coefficient of expansion for this range of temperature being 0·000904. The vapour density corresponds with the formula $C_6H_{14}O$.

The *acetate*, $CHPr^aEt \cdot OAc$, prepared by boiling the alcohol for 15 hours with acetic anhydride, is a liquid of fruity odour, boiling at 148—148·5° (at 747 mm.) and remaining mobile at -21°. Its sp. gr. is 0·8856 at 0°/0° and 0·8688 at 20°/20°.

The corresponding chloro-derivative, *ethylisopropylchloromethane*, prepared by the action of phosphorus pentachloride on the alcohol, is a colourless liquid boiling with partial decomposition at 115—116·5°, and not solidifying at -21°. The *iodide*, formed by passing hydrogen iodide into the alcohol, is a reddish liquid, readily giving off hydrogen iodide, and reacting with water with development of heat. It boils with decomposition at 142—147°, and remains liquid at -21°.

The etherification constant of the alcohol is 0·00328 for molecular proportions of carbinol and acetic anhydride in 15 vols. of benzene at 100°. The carbinol was oxidised with a 10 per cent. solution of sulphuric acid and the quantity of potassium dichromate necessary to yield 1 atom of oxygen per molecule of alcohol; the chief product of oxidation was ethyl isopropyl ketone. With a larger proportion of the oxidising agent, the products were the same as those obtained on the oxidation of ethyl isopropyl ketone.

Diethylisopropylcarbinol.—The fraction boiling at 158—161° was left for 24 hours over baryta, and then boiled with it for four hours in order to remove the ethylisopropylcarbinol. The residual liquid, diethylisopropylcarbinol, boils at 159·5—161° under a pressure of 750 mm., and becomes viscid at -21°. It has an odour resembling that of camphor, and a caustic taste. Its sp. gr. at 0°/0°

is 0.8463 and at 20°/20°, 0.8295. The corresponding chloro-derivative is a colourless liquid, which becomes brown if left over calcium chloride, and is decomposed by water, especially on heating. It cannot be distilled, as it boils with decomposition at 150—155° with rapid evolution of hydrogen chloride. The iodo-compound is a brown liquid heavier than water, by which it is easily decomposed. In the air, it fumes and smells of garlic, the vapours producing a headache. The constant of etherification of the alcohol, under the same conditions as those given above for ethylisopropylcarbinol, is 0.00056. On oxidation with 3 atoms of oxygen (from potassium dichromate and 10 per cent. sulphuric acid solution) per molecule, the alcohol yielded carbonic anhydride, acetone, and propionic, acetic, and formic acids. Amongst the products of oxidation was an unsaturated hydrocarbon identical with that obtained from the chloro-derivative by the action of alcoholic potash. This hydrocarbon proved to be *asymmetrical dimethyldiethylethylene*, $\text{CMe}_2\text{:CEt}_2$. It boils at 114.5—116.5° under 741 mm. pressure, and readily combines with bromine. The authors attempted to convert this unsaturated hydrocarbon into dimethylsecondaryamylcarbinol by heating it with fuming hydriodic acid and treating with silver oxide. The bulk of the product, however, was the original hydrocarbon, only a small quantity of a liquid boiling at 158—161° being obtained; this had the odour of a tertiary alcohol.

By means of Meyer and Locher's reaction, the authors were able to prove that a secondary alcohol is formed in the reaction between zinc ethide and acetic chloride, although only in very small quantity.

J. W.

Psyllostearyl Alcohol. By E. E. SUNDWIK (*Zeit. physiol. Chem.*, **17**, 425—430).—In Finland, in summer, the trunks of the *Alnus incana* were observed to be covered with a white powder, which was found to be the result of the presence on them of the louse, *Pyslla alni*, being a secretion from glands on its back.

A large quantity of this was collected, and a crystalline substance separated from it. It is soluble in hot chloroform, acetic anhydride, sparingly soluble in hot absolute alcohol and in ether, and not at all in cold or hot spirit. It gives no reaction of cholesterol. It melts at 95—96°, and does not give an acetyl derivative. Elementary analysis of it, and its bromine derivative, showed its simplest formula to be $\text{C}_{33}\text{H}_{66}\cdot\text{OH}$. It probably is a new member of the fatty alcohols, and the name *Psyllostearyl alcohol* is given to it.

W. D. H.

Synthesis of Sugars. By W. E. STONE (*Chem. News*, **66**, 165—166, 179—180, 194).—A valuable *résumé* of recent work on this subject.

Birotation and Hydrazone Formation of some Sugars. By H. JACOB (*Annalen*, **272**, 170—182).—A study of the change in rotatory power of solutions of sugars which have just been mixed with solutions of phenylhydrazine has shown that the hydrazone formation invariably takes place more quickly in the case of a freshly

prepared sugar solution than in that of a solution which has been kept for some time; this fact affords support to the theory that birotation is due to the combination of the solvent with the optically active substance.

The modification of glucosephenylhydrazone melting at 113—115° has, in freshly prepared aqueous solution, a specific rotatory power $[\alpha]_{D_{20}^{\circ}} = -15.3^{\circ}$; after 12—15 hours, the specific rotatory power has become constant and is then $[\alpha]_D = -46.8^{\circ}$.

Galactosephenylhydrazone has a specific rotatory power $[\alpha]_{D_{20}^{\circ}} = -21.6^{\circ}$, that of rhamnosephenylhydrazone being $[\alpha]_{D_{20}^{\circ}} = -54.2^{\circ}$; neither compound shows birotation.

A freshly prepared aqueous solution of crystalline rhamnose, $C_6H_{12}O_6 + H_2O$, is lævorotatory, but after about an hour's time the specific rotatory power has become constant at $[\alpha]_{D_{20}^{\circ}} = +8.3^{\circ}$; rhamnose which has been melted or dried for a long time does not show birotation in aqueous solution. In alcoholic solution, crystalline rhamnose shows birotation, the specific rotatory power being $[\alpha]_{D_{20}^{\circ}} = -11.4^{\circ}$ 15 minutes after solution, and becoming constant at $[\alpha]_{D_{20}^{\circ}} = -9^{\circ}$ after 16 hours. Anhydrous rhamnose also shows birotation in alcoholic solution, the initial and final values of the specific rotatory power being $[\alpha]_{D_{20}^{\circ}} = +3.4^{\circ}$ and -9° respectively.

When a freshly prepared aqueous solution of dextrose is mixed with a solution of an equal weight of phenylhydrazine in dilute acetic acid, and the mixture examined optically, the rotation is observed to change rapidly, becoming constant after about two hours; from the end value, the specific rotatory power of the hydrazone is calculated to be $[\alpha]_{D_{20}^{\circ}} = -47^{\circ}$, so that the interaction of the sugar and the hydrazine takes place quantitatively.

The rotation of a mixture of an aqueous solution of dextrose, which has been kept for 24 hours, with a solution of phenylhydrazine in dilute acetic acid also changes on keeping, but much more slowly than in the preceding case, owing to the fact that hydrazone formation takes place much more slowly; after about $5\frac{1}{2}$ hours, a constant end value, about the same as in the preceding case, is attained.

Similar results are obtained in studying the rotation of solutions of galactose and phenylhydrazine; when a freshly prepared solution of the sugar is used, the specific rotatory power becomes constant after about $2\frac{1}{2}$ hours, being then approximately $[\alpha]_{D_{17.5}^{\circ}} = -19.2^{\circ}$; as the specific rotatory power of galactosephenylhydrazone is $[\alpha]_D = -21.6^{\circ}$, it is clear that the action does not take place quantitatively.

When a galactose solution, which has been kept for 24 hours before adding the phenylhydrazine solution, is used, about $4\frac{3}{4}$ hours elapse before the specific rotatory power becomes constant at $[\alpha]_{D_{17.5}^{\circ}} = -18.4^{\circ}$.

Observations with mixed solutions of rhamnose and phenylhydrazine show that in this case also the freshly dissolved sugar combined more rapidly with the hydrazine than the sugar which had been dissolved for 24 hours; in both cases, however, a constant rotation is attained very quickly, the end value being that of rhamnosephenylhydrazone.

F. S. K.

Non-crystallisable Products of the Action of Diastase on Starch. By A. SCHIFFER (*Chem. Centr.*, 1892, ii, 825—826; from *Neu Zeit. Ruben-Zuck.-Ind.*, 29, 167—170).—The author has endeavoured to obtain Brown and Morris's maltodextrin by the action of diastase on potato starch, but without success; neither has he been able to prepare the so-called amyloins. He finds that isomaltose is formed, not maltose, and considers it probable that Brown and Morris's maltodextrin was a mixture of 67 per cent. of dextrin with 33 per cent. of isomaltose, whilst Herzfeld's maltodextrin consisted of 74 per cent. of isomaltose and 26 per cent. of dextrin.

The experiments on the dextrans did not lead to very definite conclusions. The achroödextrin obtained showed a rotatory power of $[\alpha]_D = 189.99^\circ$, and, in 3 per cent. solution, a reducing power of 12.523 per cent. on the dry substance calculated as maltose; it did not colour iodine. A non-reducing dextrin could not be obtained. The erythrodestrin obtained had a rotatory power of $[\alpha]_D = 191.27^\circ$, and a reducing power, in 4.7 per cent. solution, equivalent to 5.68 per cent. on the dry substance calculated as maltose; it gave a red coloration with iodine. The dextrans are not fermentable, and it would seem that there are only a small number, probably not more than two; at present, there is only evidence for the existence of one dextrin not giving a coloration with iodine.

Isomaltose invariably occurs amongst the transformation products of starch.
A. J. G.

Action of Dilute Acids and Alkalis on Cellulose. By E. WINTERSTEIN (*Zeit. physiol. Chem.*, 17, 391—400).—Cellulose, prepared from various sources, was subjected to the action of acids and alkalis of different strengths. The loss so produced is stated in the form of tables. The results obtained confirm the statements of earlier observers, that cellulose is but very slightly attacked by very dilute, hot, mineral acids. With alkalis (5—10 per cent.), the cellulose is considerably dissolved, but this again is confirmatory of the earlier work on the subject with impure material.
W. D. H.

Vegetable Amyloid. By E. WINTERSTEIN (*Zeit. physiol. Chem.*, 17, 353—380).—Amyloid is the name given by botanists to the constituent of cell walls, which, like starch, is coloured blue by iodine, and so differs from cellulose.

In the cotyledons, from which it was prepared in the present research, it serves as a reserve material, according to some, as a reserve cellulose. The seeds worked with were those of *Tropæolum majus*, *Pæonia officinalis*, and *Impatiens balsamina*. After its separation (the method used is fully described), it is precipitable from its aqueous solution by alcohol. The precipitate is very voluminous. It is amorphous after drying over sulphuric acid. It swells in cold, and forms an opalescent solution in hot, water. Even after the prolonged action of diastase, or boiling with water in a digester, it does not reduce Fehling's solution. The solution, after boiling in a digester, becomes clearer. $[\alpha]_D = +92-94^\circ$.

Elementary analysis gave C 43.17, H 6.08, per cent. By oxidation with nitric acid, it yields mucic acid.

In opposition to earlier investigations, it was found that, after inversion with sulphuric acid, dextrose was not formed, or only in minimal quantities; the sugars formed are two in number: one is galactose, the other a pentose, xylose.

It is difficult to say whether amyloid is a single chemical substance; it belongs to Tollens' class of polysaccharides, and especially to the saccharo-colloids.

After the extraction of amyloid from the seeds, the carbohydrate residue consists of Schulze's hemicelluloses. These substances, after inversion, were also found to yield galactose and xylose.

W. D. H.

Parent Substance of Wood Gum. By E. WINTERSTEIN (*Zeit. physiol. Chem.*, **17**, 381—390).—Wood gum, or xylan, is the material obtained from wood by extracting it with cold 5 per cent. sodium hydroxide and then precipitating with alcohol and hydrochloric acid. On inversion it yields xylose.

By treating powdered beech wood with Schulze's reagent, the residue still contains, or yields, xylan. Xylan is present in at least two modifications, one of which is destroyed by boiling with dilute acids, or by Schulze's reagent, and the other resists these. The latter parent substance of xylan appears to be cellulose. The other is probably a modification of cellulose.

W. D. H.

Molecular Compounds of Amines. By W. RUDNEW (*J. pr. Chem.* [2], **46**, 305—316).—The compounds obtained by mixing alkyl iodides with amines at the ordinary temperature are not salts of imide bases, as previously supposed by the author (*J. Russ. Chem. Soc.*, **11**, 174), but are molecular compounds of the amine and its hydriodide. The reactions studied were those between (1) tertiary butyl iodide and tertiary butylamine, which react to form the compound $C_4H_9 \cdot NH_3I, C_4H_9 \cdot NH_2$; (2) tertiary amyl iodide and tertiary butylamine, which react to form the same compound as in (1); (3) tertiary butyl iodide and tertiary amylamine, which form the compound $C_5H_{11} \cdot NH_3I, C_5H_{11} \cdot NH_2$, accompanied by a little of the compound $C_5H_{11} \cdot NH_2(C_4H_9)I$; (4) isobutyl iodide and isobutylamine, which also form $C_4H_9 \cdot NH_3I, C_4H_9 \cdot NH_2$, but a considerable proportion of the secondary amine hydriodide, $NH_2(C_4H_9)_2I$, is produced at the same time.

A. G. B.

Derivatives of Urethane. By A. ANDREOCCHI (*Real. Accad. Linc.*, 1892, i, 257—264).—The author prepares urethane by boiling carbamide nitrate with absolute alcohol and sodium nitrite under a pressure of 1.5 atmos. 70 per cent. of the theoretical yield may be obtained.

Acetylurethane is best prepared by heating urethane and acetic chloride in molecular proportion in a reflux apparatus.

Methylacetylurethane, $NMeAc \cdot COOEt$, is obtained by heating an ethereal solution of acetylurethane with sodium and methyl iodide, or by heating methylurethane and acetic chloride in closed tubes at 100—105°. It is a liquid which boils at 125—127° under 63 mm. pressure, and is very soluble in alcohol or ether. Atmospheric moisture slowly hydrolyses it, with formation of acetic acid and methylurethane.

Chloracetylurethane, $\text{NH}(\text{CO} \cdot \text{CH}_2\text{Cl}) \cdot \text{COOEt}$, is prepared by heating chloracetic chloride with urethane, or by the action of sulphuryl chloride on acetylurethane. It crystallises in prisms or rhomboidal laminae melting at $127-128^\circ$, and sublimes at 100° ; it is soluble in ether, alcohol, benzene, chloroform, or boiling water, and very sparingly so in cold water. It gives *sodio*- and *potassio*-derivatives, which are readily decomposed by water, and with sodium ethoxide yields ethylurethane.

Dichloracetylurethane, $\text{NH}(\text{CO} \cdot \text{CHCl}_2) \cdot \text{COOEt}$, is prepared by heating dichloroacetic chloride with urethane, or by heating sulphuryl chloride with chloracetylurethane or acetylurethane. It separates from hot water in rhomboidal plates, melts at 93° , and is soluble in alcohol or ether, sparingly so in cold water. It gives a *sodio*-derivative with metallic sodium.

Trichloracetylurethane, $\text{NH}(\text{CO} \cdot \text{CCl}_3) \cdot \text{COOEt}$, is an oily liquid, best prepared by heating urethane with trichloroacetic chloride. Heat converts it into a solid substance still under examination.

Acetyl-xanthamide, $\text{NHAc} \cdot \text{CSOEt}$, is obtained by heating xanthamide with acetic anhydride. It forms colourless scales, of pearly lustre, melts at 104° , and is soluble in alcohol, ether, ethyl acetate, or boiling water.

W. J. P.

Condensation of β -Diketones with Carbamide and Thio-carbamide. By P. EVANS (*J. pr. Chem.* [2], 46, 352).—When acetylacetone (1 mol.) and carbamide (2 mols.) are mixed in alcoholic solution, and 10 drops of hydrochloric acid (sp. gr. 1.19) added, crystals of the condensation product, $\text{CH}_2(\text{CMe:N} \cdot \text{CO} \cdot \text{NH}_2)_2 \cdot \text{HCl}$, separate. When four times as much hydrochloric acid is used, the compound $\text{CH}_2 < \begin{smallmatrix} \text{CMe:N} \\ \text{CMe:N} \end{smallmatrix} > \text{CO} \cdot \text{HCl}$ is formed. When sulphuric acid is substituted for hydrochloric acid, the corresponding sulphates are obtained.

Analogous compounds are prepared from acetylacetone and thio-carbamide.

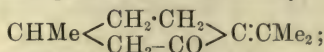
Benzoylacetone and carbamide condense with difficulty; the direct product is $\text{CPh} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CMe:N} \cdot \text{CO} \cdot \text{NH}_2$, which is split up by alkalis into $\text{CH}_2 < \begin{smallmatrix} \text{CMe:N} \\ \text{CPh:N} \end{smallmatrix} > \text{CO}$. These matters are being further investigated.

A. G. B.

Derivatives of Ketopentamethylene and Keto-hexamethylene. By F. W. SEMMLER (*Ber.*, 25, 3513—3520).—In a recent paper (this vol. i, 107), the author has shown that when tanacetogendicarboxylic acid is heated with soda-lime it yields an oil having the composition $\text{C}_8\text{H}_{12}\text{O}$, and closely resembling camphorone. From its physical properties it appears to contain a ring of carbon atoms and also an ethylene linking, the most probable formula being $\text{CH}_2 \cdot \text{CH}_2 > \text{CMe}_2$, according to which it is *isopropeneketopentamethylene*. On oxidation with dilute potassium permanganate solution, it yields a lactone, having the composition $\text{C}_7\text{H}_{12}\text{O}_3$, which boils at 145° .

under 11 mm. pressure, and melts at about the ordinary temperature. The author regards it as *δ-hydroxy-γ-isheptylic lactone*, and supposes that the carbonyl group is eliminated as carbonic anhydride, and a hydroxyl group added to each of the carbon atoms combined by ethylene linkage, the acid $\text{CMe}_2(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ then losing water, and forming the lactone $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ | \quad | \\ \text{CO} - \text{O} \end{array} > \text{CH}\cdot\text{CMe}_2\cdot\text{OH}$.

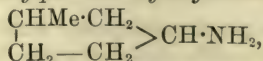
To obtain further evidence on the matter, the author has also investigated the pulegone obtained by Beckmann and Pleissner (Abstr., 1891, 936), which is probably a derivative of ketohexamethylene. In addition to the possible formulæ given by those investigators, the author gives a fourth, namely,



the presence of the isopropene group, CMe_2 , being rendered probable by the fact that it yields acetone on oxidation. If this formula is correct, the other product of oxidation should be *β-methyladipic acid*, $\text{COOH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, and it was found on investigation that this acid is formed in almost quantitative proportions. On the addition of benzene to its solution in chloroform, it separates in colourless crystals melting at 84.5° , and boiling at $210\text{--}212^\circ$ under 14.5 mm. pressure, and, like pulegone, rotates the plane of polarisation to the right. On further oxidation, the tertiary hydrogen atom in the CHMe group is oxidised to hydroxyl, the hydroxy-acid thus formed at once losing water, and forming *γ-valerolactone-γ-acetic acid*, $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ | \quad | \\ \text{CO} - \text{O} \end{array} > \text{CMe}\cdot\text{CH}_2\cdot\text{COOH}$. *β-Methyladipic acid* is readily converted into the *diethyl salt*, which has a fruity odour, and boils at 126.5° under 10 mm. pressure.

When *β-methyladipic acid* is distilled with soda-lime, it yields a liquid which smells like camphorone, and boils at $141\text{--}143^\circ$; it is a ketone and a saturated compound, and must, therefore, from its method of formation, be *β-methylketopentamethylene*, $\begin{array}{c} \text{CHMe}\cdot\text{CH}_2 \\ | \quad | \\ \text{CH}_2 - \text{CH}_2 \end{array} > \text{CO}$.

With hydroxylamine, it yields a mixture of two isomeric *oximes*, one of which melts at 81.5° , whilst the other has not yet been obtained pure. On reduction with sodium in alcoholic solution, the oximes are converted into *β-methylpentamethylenamine*,



which is a liquid smelling like the fatty amines, and boiling at 42° under 12 mm. pressure. With nitrous acid, it yields the corresponding *β-methylpentamethylenol*, $\begin{array}{c} \text{CHMe}\cdot\text{CH}_2 \\ | \quad | \\ \text{CH}_2 - \text{CH}_2 \end{array} > \text{CH}\cdot\text{OH}$, boiling at $48\text{--}50^\circ$ under 15 mm. pressure.

In conclusion, the author gives a table of constitutional formulæ, showing the relations between the compounds described in this and other papers and menthone, pulegone, camphoric acid, camphorone, &c.

H. G. C.

Products of the Dry Distillation of Birch Bark. By V. KURILOFF (*J. Russ. Chem. Soc.*, **23**, 98—101).—Birch bark, on dry distillation, gives, besides tar, a considerable quantity of an acid aqueous solution. The author has investigated this solution for acids and for bases. He first of all distilled it, and neutralised the distillate with sodium carbonate, evaporated the salt solution thus obtained to dryness, heated the residue slightly in order to drive off phenols, dissolved it in water, and filtered to remove carbonaceous matter. The filtrate was acidified with phosphoric acid, and fractionally distilled. The distillates were further subdivided by fractional neutralisation and distillation, and the acids converted into the silver salts, which were then analysed. Scarcely any difference was observed between the fractions, the amount of silver contained in the salts being in all cases only slightly less than that required by silver acetate. The aqueous solution contains 1.25 per cent. of acetic acid.

The only volatile base found was ammonia, which is present in the solution to the amount of 0.73 per cent. J. W.

Preparation of Chloroacetic acid. By A. RUSANOFF (*J. Russ. Chem. Soc.*, **23**, 222—223).—The chlorination of acetic acid may be readily effected by mixing the glacial acid employed with from $\frac{1}{12}$ th to $\frac{1}{15}$ th of its weight of red phosphorus. A rapid current of chlorine is passed into the mixture at 100°, the absorption being very complete. On cooling, the liquid solidifies to a white, crystalline mass, which is almost pure monochloroacetic acid. With the above proportion of phosphorus, the quantity of chloro-acid obtained is about equal to the quantity of acetic acid taken. J. W.

Compounds of Copper Acetate with Ammonia and with Pyridine. By F. FOERSTER (*Ber.*, **25**, 3416—3422).—*Copper acetate ammonia*, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{NH}_3$, is prepared by adding an excess of alcoholic ammonia to an alcoholic solution of copper acetate (a certain quantity of copper oxide is formed when aqueous solutions are employed); after distilling off the excess of alcohol, the salt separates, and when recrystallised from alcohol, it is obtained in anhydrous, short, violet prisms or octahedra. It may be dried over sulphuric acid in a vacuum. Schiff (*Annalen*, **123**, 43) has described a hydrate of this compound, crystallising with 2 mols. H_2O , which he obtained by allowing an aqueous ammoniacal solution of copper acetate to evaporate at the ordinary temperature. The author finds that the anhydrous compound separates from concentrated aqueous solutions, whilst a hydrate, crystallising in blue needles with $2\frac{1}{2}$ mols. H_2O , and having crystallographic relations agreeing with those observed by Schiff for his compound, is obtained from dilute solutions. The copper acetate ammonia gradually loses ammonia in moist air, and deliquesces; it dissolves in water, forming a deep blue solution, which on dilution yields a bright blue jelly; the latter changes after a time into a fine powder, consisting of a basic copper acetate. It deliquesces rapidly in contact with aqueous ammonia, but undergoes no chemical change. When dry gaseous ammonia

is passed over anhydrous copper acetate, or better over the above described anhydrous copper acetate ammonia, it is absorbed with the evolution of heat. In the second case, the colour of the compound changes to blue, and a compound, probably $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{NH}_3$, is produced; it, however, quickly dissociates in the air into ammonia and the compound $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{NH}_3$; a compound containing less ammonia than the latter could not be obtained.

Copper acetate pyridine, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{C}_5\text{NH}_5$, separates in lustrous, pure blue, six-sided tables, when pyridine is added to an aqueous or alcoholic solution of copper acetate, and the mixture evaporated. It remains unaltered over concentrated sulphuric acid in a vacuum, but undergoes slight decomposition when heated at 100° . It may be crystallised from hot water, and is only slightly decomposed when boiled with that solvent for a long time; it, however, suffers more decomposition when dissolved in boiling alcohol. When finely pulverised copper acetate is triturated with an excess of pyridine, a blue compound, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{C}_5\text{NH}_5$, is obtained; it gradually loses 3 mols. of pyridine on remaining in the air.

The blue liquid used for filling thermometer tubes often consists of an alcoholic solution of copper acetate ammonia, and when the instrument is constructed of bad glass, the free alkali causes a precipitation of basic copper acetate, or copper oxide. The means of preventing such precipitations will form the subject of a future communication.

Crystallised copper acetate (1 mol. H_2O) remains constant in weight when kept over concentrated sulphuric acid in a vacuum, as stated by Roux (*Annalen*, **60**, 316), but it is slowly dehydrated at 100° , more rapidly at 105° ; the anhydrous salt is green.

A. R. L.

The Behaviour of α -Amidopropionic acid at High Temperatures. By E. DRECHSEL (*Ber.*, **25**, 3502—3504).—When a solution of α -amidopropionic acid in concentrated phosphoric acid is distilled, water at first comes over; the temperature then rises to 220 — 230° , decomposition sets in, and aldehyde, carbonic oxide, and ammonia are formed.

E. C. R.

Crotonic acids and their Derivatives. By A. MICHAEL and O. SCHULTESS (*J. pr. Chem.* [2], **46**, 236—266).—The details of the methods for preparing the crotonic acids given in this paper do not materially differ from those already published. Wislicenus and others (*Abstr.*, 1887, 655; 1889, 236) have investigated the chlorination and bromination of crotonic and isocrotonic acids in carbon bisulphide and, in the case of isocrotonic acid, have obtained liquid acids which were regarded as $\alpha\beta$ -isodichloro- and $\alpha\beta$ -isodibromobutyric acids mainly on the ground that they were convertible into α -chloro- or α -bromo-crotonic acid, respectively, by the action of sodium hydroxide. Beside these, small quantities of the solid dichloro- and dibromo-butyric acids were obtained, and their formation was attributed to the presence of crotonic acid in the isocrotonic acid used. In their study of the same subject, the authors used

chloroform and carbon tetrachloride as solvents for chlorination experiments, and carbon bisulphide for bromination experiments; the products crystallised in all cases, and only in the chlorination experiments was any notable quantity of oily product obtained. They are, therefore, unable to confirm the existence of the liquid acids above referred to, and attribute their supposed formation to the presence of products of the action of the halogens on the carbon bisulphide or its impurities, which would be specially liable to occur in absence of bright light, and would hinder the crystallisation of the acids. Nor is Wislicenus correct in his statement as to the action of sodium hydroxide on the products in question (see above); a mixture of the normal and iso-acids is produced in each case, and in that of the chlorination product the mixture contains more of the iso- α -chloro-crotonic acid.

The above experiments were performed with an isocrotonic acid which, although containing less crotonic acid than that used by Wislicenus, was not perfectly pure, and the authors' attention was turned to the obtainment of a pure acid. When this acid was prepared, its chlorination and bromination gave results virtually identical with those outlined above. The purification was effected by means of the difference in solubility of the sodium salts in alcohol. At 11° 1 part of sodium crotonate dissolves in 380 parts of absolute alcohol, whilst 1 part of sodium isocrotonate dissolves in 16 parts.

In the aqueous mother liquor of the crotonic acid recovered from the crude isocrotonic acid by the new process, there was found a small quantity of tetrolic acid (m. p. 76°) which was at first mistaken for a new acid owing to the fact that it crystallises from light petroleum, together with crotonic acid (m. p. 72°), in prisms which melt at 83°; this is a notable instance in which a mixture of two substances melts at a higher temperature than does either constituent. The discovery that tetrolic acid is a secondary product of the action of sodium amalgam on β -chlorisocrotonic acid elucidates a difficulty noted by Geuther (*Zeit. Chem.*, 1871, 244) who, when reducing β -chlorocrotonic acid (m. p. 94°), obtained crystals which melted at 79° until they had been several times recrystallised, when the melting point dropped to 72°; a repetition of Geuther's experiments resulted in the isolation of tetrolic acid (compare Fittig and Clutterbuck, *Abstr.*, 1892, 961). It was not found possible to avoid the formation of tetrolic acid during the reduction of β -chlorisocrotonic acid.

Pure isocrotonic acid boils at 74° under 15 mm. (bath at 85°) and at 78·5° under 20 mm. (bath at 90°); the *silver salt* is a white, curdy precipitate, which crystallises from hot water in lustrous needles. When the acid is heated for 36 hours in a sealed bulb at 100°, it undergoes no change; under the same conditions at 136°, 34 per cent. of it is converted into the solid crotonic acid, whilst at 162° and 182°, 66 per cent. and 67·5 per cent., respectively, are so converted (compare Alberti, *Ber.*, 9, 1194); in the presence of a trace of iodine, the conversion takes place to a slight extent at 100°. Comparative experiments were made concerning the elimination of chlorine from β -chlorocrotonic acid (m. p. 94°) and β -chlorisocrotonic acid (m. p. 61°) by 10 times their weight of 30 per cent. sodium hydroxide solu-

tion, care being taken to avoid rise of temperature; it was found that, after 14 days, the β -chlorocrotonic acid had lost 95 per cent., and the β -chlorisocrotonic acid 88 per cent. of its chlorine. The influences of time and concentration were also studied, and the results are tabulated.

Experiments are detailed which prove that $\alpha\beta$ -dichlorobutyric acid (m. p. 63°) yields, contrary to Wislicenus' statements (Abstr., 1887, 655; 1889, 236), a mixture of α -chlorocrotonic and α -chlorisocrotonic acids when treated with either warm or cold sodium hydroxide. When $\alpha\beta$ -dibromobutyric acid is thus treated, only some 3.5 per cent. of α -bromocrotonic acid is produced, the rest being α -bromisocrotonic acid (m. p. 92°). Melikoff's experiment of heating α -chlorocrotonic acid with hydrochloric acid (compare Abstr., 1886, 1008) was repeated; the $\alpha\beta$ -isodichlorobutyric acid thus obtained crystallises in prisms, melts at 78° (Melikoff gave 72 — 73° ; Abstr., 1892, 296), and distils at 131.5° under 20 mm. (bath at 145°). The isolation of this second solid $\alpha\beta$ -dichlorobutyric acid is evidence that Wislicenus' liquid acid has no existence.

$\alpha\beta$ -Isodibromobutyric acid was prepared by heating α -bromocrotonic acid with hydrobromic acid at 100° in a sealed tube for 20 hours; it crystallises in small needles, melts at 58 — 59° , and is more soluble than the known acid (m. p. 87°). With alkalis, it yields a mixture of α -bromocrotonic acid and α -isobromocrotonic acids. $\alpha\beta$ -Dibromobutyric acid (m. p. 87°) is partly converted into this acid (m. p. 58 — 59°) when heated with hydrobromic acid.

As is already known (Abstr., 1883, 969), β -chlorocrotonic acid is partially converted into β -isochlorocrotonic acid when heated; but α -isobromocrotonic acid is entirely converted into α -bromocrotonic acid when heated in boiling xylene.

A. G. B.

Formation of Solid Crotonic acids by the Reduction of α -Isobromo- and α -Isochloro-crotonic acids. By A. MICHAEL (*J. pr. Chem.* [2], 46, 266—272).—The author quotes experiments which show that α -isobromocrotonic acid is converted almost entirely into solid crotonic acid when reduced by sodium amalgam, whether in acid or alkaline solution. α -Isochlorocrotonic acid also yields much more solid than liquid crotonic acid when similarly reduced. This repetition (compare Abstr., 1888, 1176) is rendered necessary by Wislicenus' criticisms (*Annalen*, 248, 352).

A. G. B.

Addition of Bromine and Chlorine to Solid Crotonic acid. By Mrs. H. A. MICHAEL (*J. pr. Chem.* [2], 46, 273—285; compare preceding abstracts).—The experiments detailed in this paper were undertaken as part of the controversy between Michael and Wislicenus, and have special reference to the remarks of the latter in *Annalen*, 248, 281. The tabulated results show that the addition of chlorine and bromine to solid crotonic acid is accompanied by fewer secondary reactions when allowed to proceed rapidly in a well cooled solution exposed to direct sunlight. The $\alpha\beta$ -dihalogen butyric acid produced, when the reaction was normal, was accompanied by some

10 per cent. of the iso-acid in the chlorination experiments, and by some 3 per cent. in the bromination experiments. A. G. B.

Brom-additive Products of Angelic and Tiglic acids. By J. WISLICENUS (*Annalen*, 272, 1—99).—Fittig (Abstr., 1891, 39) attempted to show that the results obtained by the author and Pückert (Abstr., 1889, 587), in studying the action of bromine on angelic acid, were inaccurate; he claimed to have proved that tiglic acid dibromide, and not angelic acid dibromide, is produced by the action of bromine on angelic acid, and at the same time he made several statements reflecting very seriously on the author. The first portion of the paper is devoted to a refutation of these statements.

In preparing angelic and tiglic acids from various samples of Roman oil of chamomile by several different methods, it was found that, not only was the composition of the oil very variable, but that the yield of the two acids depended very much on the method of treatment; the total yield of crude, oily acid product, obtained by hydrolysing the oil with alcoholic potash, and weighed moist, was always between 49 and 51 per cent. of the oil, but the relative quantities of the several constituents were very variable. Many oils contained very little methacrylic acids, others a great deal. The fraction of the oily acid product which boiled above 175° always contained angelic acid as principal constituent; tiglic acid, if present, occurred in smaller quantities, and sometimes seemed to be absent altogether from the original oil. The yield of tiglic acid increased with the quantity of potash employed in hydrolysing, with the duration of the heating, and even more with the duration and frequency of the subsequent fractional distillation, the quantity of angelic acid becoming correspondingly smaller. When a good yield of angelic acid is desired, a preliminary partial separation of the two acids by means of their calcium salts is to be recommended, although this method is not so satisfactory as would appear from Pagenstecher's description; when tiglic acid is also required in quantity, Kopp's method of preparation is to be preferred.

From observations made with a large number of compounds, it has been found that, in order that the formation of additive products of unsaturated compounds may take place in the simplest manner, and without intramolecular change, the reaction must be carried out at the lowest possible temperature, and light excluded as far as possible; further, that the halogens and halogen acids, which are to be combined with the unsaturated compound, must always be present in large excess.

Under these conditions, and employing pure and dry substances and solvents, the pure dibromo-additive products of angelic and tiglic acids can be easily prepared.

The preparation of these compounds is then described in great detail. Briefly, the method was to slowly add, with frequent shaking, very small quantities of a solution of the acid in carbon bisulphide to a solution of not less than $1\frac{1}{2}$ mols. of bromine also dissolved in carbon bisulphide, in absence of moisture and in a very dim light, the temperature being kept below 10°; after the whole of the acid was

added, an operation which required $1\frac{1}{2}$ to 2 hours, the mixture was kept over night, and the carbon bisulphide and excess of bromine then evaporated in a stream of dry air, one vessel being used for the whole process. Under these conditions, which will hereafter be referred to as normal, the yield of crude tiglic acid dibromide is only a few tenths per cent. below the theoretical, a trace of some substitution or decomposition product being also formed with evolution of hydrogen bromide; the yield of crude angelic acid dibromide, on the other hand, is rather more than the theoretical, owing to the difficulty of expelling all the carbon bisulphide.

The two acids show, even up to this point, a totally different behaviour. The solution of the tiglic acid dibromide begins to crystallise long before the whole of the carbon bisulphide is evaporated, and a snow-white dibromo-derivative, identical with the compound described by Pagenstecher (Abstr., 1879, 455), as was found by Pückert, is obtained. The solution of the angelic acid dibromide, on the other hand, yields, on evaporation, a brown oil, but, on continuing to pass a stream of dry air for a long time, crystallisation begins at the edges and gradually proceeds, accompanied by a continual decrease in weight; when, however, the oil is placed over soda-lime under reduced pressure, it soon froths up, gradually becomes thick, and finally solidifies to a hard, yellow mass, which still smells of bromine and carbon bisulphide.

The tiglic acid dibromide, after recrystallisation from light petroleum (b. p. 60°), melts at $87-88^{\circ}$, and does not liquefy on treatment with water.

The crude crystalline angelic acid dibromide is best freed from most of its carbon bisulphide by repeatedly treating it with petroleum pentane (b. p. $25-33^{\circ}$), and evaporating the latter in a rapid stream of air; it can then be recrystallised from warm petroleum pentane (b. p. $33-39^{\circ}$). When this purification is repeatedly carried out, in absence of moisture, and the crystals then freed from petroleum and carbon bisulphide in a desiccator under reduced pressure, a compound is obtained melting constantly at $86.5-87^{\circ}$, but the least trace of moisture lowers the melting point very considerably.

As the yield of pure substance is more than 90 per cent. of the crude product, further quantities of the pure compound being obtainable from the mother liquors, the author is absolutely convinced that a homogeneous substance, differing considerably in properties from tiglic acid dibromide, can be obtained from angelic acid in the manner described.

The two dibromides show a considerable difference in behaviour in passing from the liquid to the solid condition. The tiglic acid dibromide solidifies to an opaque, crystalline mass. The angelic acid dibromide forms an amorphous, resinous mass which becomes crystalline after some time; this amorphous dibromide is much more readily soluble in light petroleum than the crystalline variety, and on quickly evaporating its almost saturated solution, it is again deposited in an amorphous condition. When the solution of the amorphous substance is kept in a closed vessel, it begins to deposit crystals after some time, and, if the mother liquors are evaporated soon after the

first separation of crystals occurs, an amorphous, gum-like mass is obtained, in which crystals are embedded; if, on the other hand, the mother liquors are not evaporated until after long keeping, only the crystalline dibromide is deposited.

The most striking difference in properties between the two dibromides is in their behaviour with water. Whereas tiglic acid dibromide is sparingly soluble in, but is not otherwise changed by, water, and separates from its aqueous solution in crystals, angelic acid dibromide slowly liquefies when kept in an atmosphere saturated with aqueous vapour, and is immediately converted into a highly refractive oil in contact with water. This oil seems to be an unstable compound, probably of the composition $C_5H_{10}Br_2O_3$; it decomposes in moderately dry air or when treated with concentrated hydrochloric acid, yielding crystals of the dibromide, but, when kept at 0° in a closed vessel, it does not show the least signs of crystallising.

The solubility of the two dibromides in water, benzene, carbon bisulphide, and light petroleum is also very different, as was proved by careful determinations at various temperatures; the following table shows the solubility in 100 parts of the several liquids.—

	Water.	Petroleum pentane.	Benzene.	Carbon bisulphide.
Angelic acid di- bromide	2.46 at 16° 2.63 at 20°	35.22 at 8° 138.9 at 20°	437.74 at 14.5° 542.52 at 21.5°	315.27 at 3° 472.29 at 15.5°
Tiglic acid di- bromide	0.94 at 16° 1.01 at 20°	6.06 at 8° 11.89 at 20°	72.99 at 14.5° 87.28 at 21.5°	45.26 at 3° 69.98 at 15.5°

The homogeneity of the angelic acid dibromide was carefully tested by well shaking a weighed quantity of various samples of the compound with successive small quantities of water; the solubility remained absolutely constant, and not a trace of a crystalline powder (tiglic acid dibromide) could be detected in the small quantity of oil remaining undissolved after many treatments (compare Fittig, *loc. cit.*); this oil dissolved on adding sufficient water, the total quantity of water used being rather more than that calculated from the solubility of angelic acid dibromide.

When a mixture of the two dibromides is repeatedly extracted with successive small quantities of water, the angelic acid dibromide first passes into solution, its solubility, determined experimentally, being practically the same as when the pure substance alone is used; after about six extractions, under the conditions employed, the oily residue solidifies, and the extracts then contain tiglic acid dibromide in quantities corresponding very closely with those calculated from the normal solubility.

The solubility of the angelic acid dibromide is, however, slightly diminished by the presence of tiglic acid dibromide; when a saturated aqueous solution of pure angelic acid dibromide is shaken with a relatively very small quantity of tiglic acid dibromide, the latter first

becomes pasty and then changes to a turbid oil, owing to the separation of a small quantity of oily angelic acid dibromide.

The solubility of tiglic acid dibromide is diminished to an even greater extent by the presence of angelic acid dibromide, more than five-sixths of the compound being precipitated from its saturated aqueous solution as a crystalline powder on adding angelic acid dibromide to saturation, and then shaking well.

A further difference in the behaviour of the two dibromides is observed when they are triturated with tiglic acid in absence of moisture; the angelic acid dibromide forms an oily mixture with the tiglic acid, whereas the tiglic acid dibromide gives a powdery mixture; both the dibromides give an oily mixture when triturated with angelic acid.

Crystallographic measurements of the two dibromides, made by Fock with crystals obtained from petroleum pentane solution, showed slight but distinct differences between the two compounds.

When the above-mentioned normal conditions under which angelic acid is converted into its dibromide are not strictly adhered to, a considerable quantity of tiglic acid dibromide is formed: this compound may, in fact, be produced in such large quantities that a careless examination would lead to the conclusion that it was the sole product.

Numerous experiments were made in order to determine the influence of temperature, order of mixing, &c., on the course of the reaction.

In the first place, it was found that at temperatures above 25° , other conditions remaining normal, a considerable quantity of tiglic acid dibromide is formed; at $25-29^{\circ}$, of every 100 parts of angelic acid, at the most 14.5 parts are converted into tiglic acid dibromide; at $35-40^{\circ}$, about 28 parts. Tiglic acid dibromide is also formed when the carbon bisulphide solution of the bromine is added to that of the angelic acid, instead of *vice versa*, other conditions remaining normal; at $16-20^{\circ}$, of every 100 parts of angelic acid about 35.9 parts are converted into tiglic acid dibromide; at $25-29^{\circ}$, about 46.7, and at $34-40^{\circ}$, about 68.7 parts.

The influence of bright light and of the order of mixing, on the course of the reaction are even more striking. When a carbon bisulphide solution of bromine in slight excess is slowly added in small quantities at a time to a carbon bisulphide solution of angelic acid, kept below 5° , but exposed to bright sunlight, each addition of bromine, except the last two, being made only after the solution has become colourless, the yield of tiglic acid dibromide varies from 88.74 to 92.8 per cent. of the crude brominated product, seemingly according to the intensity of the light; when, on the other hand, the solution of the acid is added to that of the bromine, the temperature remaining the same, the yield of tiglic acid dibromide is only 47.6 per cent. of the crude product, even when the operation is carried out in sunlight.

It is clear, therefore, that the principal cause to which the formation of tiglic acid dibromide is due must be active during and not after the combination of the angelic acid with the halogen; special

experiments showed that angelic acid dibromide is not transformed into the isomeride when its saturated solution in petroleum pentane is heated at 50° , or exposed for a long time to direct sunlight.

When tiglic acid is treated with bromine under the normal conditions, the product is invariably pure tiglic acid dibromide; when, however, the temperature is $25-29^{\circ}$, a small quantity (about 1.35 per cent.) of the crude product consists of angelic acid dibromide. The effect of adding the carbon bisulphide solution of the acid to that of the bromine is much more marked; at $18-20^{\circ}$, of every 100 parts of tiglic acid 3.77 parts, and at $43-45^{\circ}$, 7.94 parts, are converted into angelic acid dibromide when the reaction takes place in a very dim light; whereas in sunlight, even at 0° , the quantity of angelic acid dibromide varies from 7.43 to 11.58 per cent. of the mixed products, seemingly according to the intensity of the light.

In most of Fittig's experiments, it is definitely stated that the carbon bisulphide solution of bromine was added to that of the acid; and in all cases, with one exception, conditions favourable to the production of tiglic acid dibromide were dominant. In the exceptional case referred to, working by gaslight, the carbon bisulphide solution of the angelic acid was very slowly added to that of excess of bromine; as the next morning the solution was still deeply coloured with bromine, the mixture, cooled all the time in ice-water, was kept for three days exposed to diffused sunlight. Under these conditions, it was stated, the weight of pure tiglic acid dibromide isolated amounted to more than half that of the crude brominated product.

As this result was at variance with the author's observations, he repeated the experiment under exactly the same conditions as those employed by Fittig; it was found that the quantity of tiglic acid dibromide formed is certainly not as much as 5 per cent. of the crude brominated product.

The explanation of Fittig's results is to be sought for in the following facts:—Firstly, he used only a slight excess of bromine; secondly, the solutions were not only mixed at a low temperature, but were also kept at a low temperature over night; thirdly, the next morning the solutions were exposed to diffused, moderately bright sunlight. The first two conditions retard combination to such an extent that, even after keeping over night, the solution still contains angelic acid, which, on exposing the mixture to diffused sunlight, combines with the bromine present in only slight excess to form tiglic acid dibromide.

Although, it is true, Fittig worked under conditions favourable to the formation of tiglic acid dibromide, his statements relative to the yield of this compound are very untrustworthy; a sample of Fittig's own preparation, stated to consist essentially of tiglic acid dibromide, was examined by the author and found to contain 81.75 per cent. of angelic acid dibromide, and only 18.25 per cent. of the isomeride; a sample stated to be pure tiglic acid dibromide was found to contain as much as 25.57 per cent. of angelic acid dibromide.

Another fact which vitiated Fittig's results is, that he distilled the angelic acid employed in the bromination experiments; when pure

angelic acid (8—10 grams) is quickly distilled, more than 1.5 per cent. is converted into tiglic acid.

The sample of angelic acid dibromide prepared by Pückert, which, according to Fittig, contained calcium and "was wanting in all the properties of a pure compound" (*loc. cit.*) was carefully examined; it was found to contain calcium equivalent to 0.5 per cent. of calcium chloride, or 2.5 per cent. of the calcium salt of angelic acid dibromide, that is to say, a quantity too small to appreciably affect Pückert's analytical results. Two fresh samples of angelic acid dibromide were prepared, exactly as described by Pückert; they were found to contain only about 10 per cent. of tiglic acid dibromide, so that the sample examined by Fittig certainly could not have consisted principally of this compound, as was stated to be the case.

The bye-product obtained by Fittig in the preparation of angelic acid dibromide (*loc. cit.*), which was stated to have great influence on the properties of the tiglic acid dibromide, is an oily mixture or compound of angelic acid dibromide with angelic acid or tiglic acid (see above), and is formed in larger quantity the dimmer the light and the smaller the quantity of bromine used; when only 2 mols. of bromine are employed to 3 mols. of the acid, the experiment being carried out in a dim light, hardly any crystalline product is obtained; working in a bright light, solid mixtures consisting essentially of tiglic acid dibromide and tiglic acid are obtained, the angelic acid, under these conditions, being converted into the isomeride.

In order to investigate the nature of the bye-products formed in the preparation of angelic acid dibromide under the normal conditions, a large quantity (200 grams) of the pure acid was treated at various times in the normal manner; after separating the pure angelic acid dibromide as completely as possible, an operation which lasted about a year, nearly 11 grams of an oil, which appeared still to contain not inconsiderable quantities of angelic acid dibromide, remained. On treating this oil with sodium carbonate, about 1 gram of a coloured, neutral liquid containing bromine, probably a polymeride of bromobutylene, remained undissolved; the solution, on distillation, gave 1.65 grams of bromobutylene, a quantity equivalent to 3.1 grams of angelic acid dibromide, and from the residue about 0.2 gram of tiglic acid was isolated. The quantity of substance unaccounted for amounted therefore to little more than 0.67 per cent. of the crude bromination product, and may doubtless be put down as unavoidable loss incurred in the examination of the oil.

These experiments prove that a readily soluble substance, which, according to Fittig, has, even when present in very small quantities, a remarkable influence on the properties of tiglic acid dibromide, is not formed by the action of bromine on angelic acid.

Although it is impossible to fulfil Fittig's request, to submit to him a pure isomeride of tiglic acid dibromide "which passes into tiglic acid dibromide when its cold, freshly prepared solution is kept in a desiccator," the author considers that his present work has shown the existence and established the properties of angelic acid dibromide with as great a degree of certainty as has been done in the case of any other organic compound.

The reason that Pückert first observed the existence of this isomeride of tiglic acid dibromide, and that its discovery was not made years ago in Fittig's laboratory, is simply the result of accidental circumstances. In the Leipzig laboratory the draught cupboards happen to have been built between the windows, and are only dimly lighted; in the Strasburg laboratory, on the other hand, they are placed in the windows and receive bright daylight. Had the former been constructed like the latter, it is probable that angelic acid dibromide would not yet have been discovered. F. S. K.

Constitution of Angelic and Tiglic acids. By I. KONDAKOFF (*J. Russ. Chem. Soc.*, **23**, 178—217; compare Abstr., 1892, 1304).—The alcohol (b. p. 131—133°) from "mixed amylenes" yields, on oxidation with dilute potassium permanganate, acetic, propionic, and glyoxylic (?) aldehydes, and an unsaturated aldehyde C_5H_8O ; formic, acetic, propionic, and glycollic acids, along with a non-volatile dihydroxy-acid $C_5H_{10}O_4$, and a non-volatile neutral substance $C_5H_{12}O_3$, which is pentenylglycerol. This glycerol, on oxidation in the same manner, gives acetic, propionic, and glyoxylic aldehydes, acetic acid, propionic acid, oxalic acid, and the dihydroxy-acid; on oxidation with chromic mixture, it yields fumaric, acetic, and propionic acids. The author considers that these results show the alcohol to consist of two isomerides $CH_2:CET\cdot CH_2\cdot OH$ and $CH_2:CME\cdot CH_2\cdot CH_2\cdot OH$, from the former of which are derived the aldehyde $CH_2:CET\cdot CHO$, and the propaldehyde. The dihydroxy-acid and the glycerol are probably mixtures of isomerides derived from both isomeric alcohols. The aldehyde C_5H_8O gives an acid $C_5H_8O_2$, probably α -ethoxyacrylic acid, which, when heated with sulphuric acid for 10 hours in a sealed tube at 100° is converted into tiglic acid.

Amongst the products of oxidation of angelic acid by potassium permanganate were found citramalic acid and glycollaldehyde. No glyceric acid was found amongst the oxidation products of tiglic acid. The author draws the conclusion that angelic acid is not α -ethylacrylic acid, but α -methylisocrotonic acid, and that the isomerism between angelic and tiglic acids is occasioned by a structural difference between them, and is not a case of geometrical isomerism. J. W.

Constitution of Glyoxylic acid. By R. OTTO and J. TRÖGER (*Ber.*, **25**, 3425—3429).—When potassium glyoxylate is added by degrees to a large excess of thiophenol, through which a steady current of hydrogen chloride is being passed, *dithiophenylacetic acid*, $COOH\cdot CH(SPh)_2$, is formed with development of heat. It forms faintly yellowish prisms (probably monosymmetric), melts at 104—106°, and is readily soluble in alcohol and ether, but insoluble in water. In the light of the experiments of Baumann and his pupils, on the formation of mercaptals from aldehydes and mercaptans, this result serves to show that glyoxylic acid is to be regarded as formylcarboxylic acid, $COH\cdot COOH$, and not as dihydroxyacetic acid. Diphenylsulphonemethane (Fromm, Abstr., 1890, 56) is obtained when dithiophenylacetic acid is treated with potassium permanganate

solution and a few drops of dilute sulphuric acid in the presence of benzene. The authors find that this compound melts at 120—121°.

A. R. L.

Dibromosuccinic acids. By W. LOSSEN (*Annalen*, 272, 127—139).—When dibromosuccinic acid is boiled for about 10 minutes with normal soda or potash, it is almost completely converted into the corresponding salt of acetylenedicarboxylic acid, with formation of sodium or potassium bromide; when more concentrated (about 12½ per cent.) soda is used, part of the sodium acetylenedicarboxylate undergoes decomposition into sodium propargylate and sodium carbonate with evolution of carbonic anhydride.

Dibromosuccinic acid is also decomposed by normal soda at the ordinary temperature, by boiling normal barium hydroxide, and by boiling milk of lime, the principal product being a salt of acetylenedicarboxylic acid in all cases; in one experiment, oxalic acid seemed to be formed in very small quantities when milk of lime was used.

Isodibromosuccinic acid behaves like dibromosuccinic acid towards boiling normal soda and boiling milk of lime, but is rather more readily decomposed.

Tartaric acid is not formed from either of the above mentioned acids under the conditions stated.

F. S. K.

Action of Sodium Ethoxide on Ethyl Dibromosuccinate.

By A. MICHAEL and C. C. MAISCH (*J. pr. Chem.*, [2], 46, 233—235).

—Pim (Abstr., 1888, 1058) stated that the product of this reaction is ethyl acetylenedicarboxylate (this vol., i, 145). The authors find, however, that the product boils at 149—149·5° (20 mm.; temp. of bath 180°) and is destitute of the penetrating odour characteristic of ethyl acetylenedicarboxylate; they deduce, from their analyses of the compound, that it is ethyl diethoxysuccinate.

A. G. B.

Addition of Chlorine to Polybasic Unsaturated Fatty Acids.

By A. MICHAEL and G. TISSOT (*J. pr. Chem.*, [2], 46, 381—399; compare this vol., i, 134).—When a 10 per cent. solution of chlorine in carbon tetrachloride acts on a solution of dimethylmaleic anhydride in the same solvent for three days in a good light, a quantitative yield of α -dichloro-symmetrical-dimethylsuccinic anhydride (Abstr., 1890, 957) is obtained; it has a tear-exciting odour, is easily soluble in most solvents, and melts, with sublimation, at 159—160°. Its identity is settled by its easy conversion by water into the corresponding dichloradipic acid (Abstr., 1885, 753).

Citradichloropyrotartaric acid is formed when chlorine acts on citraconic anhydride in carbon tetrachloride in sunlight, and the product is treated with water. It crystallises, melts at 119—120° with decomposition, and dissolves in alcohol, ether, acetone, and ethyl acetate. By destructive distillation, it is split up into chlorocitraconic anhydride, hydrogen chloride, and water. When the acid is heated with water, carbonic anhydride, propaldehyde, chloromethylacrylic acid (m. p. 59°), chlorocitraconic anhydride (m. p.

98°—100°), and chlorocitramalic acid (m. p. 139°) can be isolated from the solution. The *barium* (with 4 mols. H_2O) and *lead* (with 4 mols. H_2O) chlorocitramalates were prepared. Swarts (*Jahresber.*, 1873, 582) claimed to have prepared citradichloropyrotartaric acid by the action of chlorine on an aqueous solution of citraconic anhydride in sunlight; in view of the ease with which the acid is decomposed by water, this does not seem possible.

Chloromesaconic acid can be prepared by acting on citradichloropyrotartaric acid with alkalis. It crystallises in rhombic tables, sublimes gradually at 150°, melts at 208°, solidifies again at 200°, and dissolves in water, but only sparingly in benzene and chloroform. The *silver* and *barium* (with 4 mols. H_2O) salts were prepared.

Mesadichloropyrotartaric acid is obtained as its *chloride*, $\text{C}_5\text{H}_6\text{Cl}_4\text{O}_2$, (b. p. 105—106° at 21 mm.) when mesaconic chloride is treated with chlorine in carbon tetrachloride in sunlight; the chloride is decomposed by water and the acid isolated by extraction with ether. It crystallises in microscopic prisms, melts at 123°, and is less hygroscopic than the citra-acid. With water and alkalis, it behaves like the citra-acid, but is rather more easily decomposed by the former.

Allo- $\alpha\beta$ -dichlorosuccinic anhydride is the product of the action of chlorine on maleic anhydride in carbon tetrachloride in sunlight; it forms silvery crystals, melts at 95°, and is very hygroscopic, readily passing into the corresponding *acid*, which crystallises in large, transparent crystals, and melts at 175° with decomposition; when heated with water it passes into chlorofumaric acid (m. p. 190—191°).

$\alpha\beta$ -Dichlorosuccinic chloride is similarly produced from fumaric chloride; it is a thick, colourless oil having a tear-exciting odour, and boils at 105—106° (45 mm.). By the prolonged action of water, it is converted into the corresponding *acid*, which crystallises in colourless prisms, melts at 215°, and is less soluble in water than the *allo-acid*; by alkalis it is converted into chlorofumaric acid, together with a small quantity of an acid of lower melting point, probably chloromaleic acid.

In conclusion, the authors compare the above results with the decomposition of the corresponding bromo-acids by water as worked out by Fittig and Krusemark (*Annalen*, 206, 1), who did not obtain bromomethylacrylic acid from citradibromopyrotartaric acid. How this affects the Michael-Wislicenus controversy is briefly discussed.

A. G. B.

Action of Chlorides of Bibasic Acids on Ethyl Sodiocyanacetate. By T. MULLER (*Compt. rend.*, 115, 953—955).—On evaporating the ether used in washing the ethyl succinocyanacetate obtained by the action of succinic chloride on ethyl sodiocyanacetate, a yellowish substance is left, consisting of a mixture of ethyl cyanacetate and ethyl succinodicyanacetate, from which the latter may then be separated.

Ethyl succinodicyanacetate, $\text{C}_2\text{H}_4[\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{COOEt}]_2$, crystallises in small tufts of slender, white needles, and melts at 135—136°. It is hydrolysed by boiling water into succinic acid and ethyl cyan-

acetate, and is a true acid, decomposing alkaline carbonates. The sodium, silver, and cuprous salts are described. JN. W.

Addition of Bromine to Acetylenedicarboxylic acid and its Ethyl Salt. By A. MICHAEL (*J. pr. Chem.* [2], **46**, 210—233).—Bandrowski (Abstr., 1880, 160) found that dibromofumaric acid is the chief product of the action of bromine on acetylenedicarboxylic acid. This observation did not fall in with Wislicenus' theory as to the arrangement of atoms in space (Abstr., 1888, 1058), so that this chemist further investigated the reaction, and has stated (*Annalen*, **259**, 78) that, if the action of hydrogen bromide be excluded, dibromomaleic acid is mainly produced. The author has shown (*J. pr. Chem.* [2], **37**, 34) that all acetylene derivatives formed by the displacement of the acetylene hydrogen by two negative organic radicles yield two alloisomeric dibromo-additive products; the present research proves that the dicarboxylic acid is no exception to this rule. Acetylenedicarboxylic acid melts at 178—179° (not 175°), and reacts rapidly with bromine in aqueous solution when exposed to bright diffused light, without the vigorous evolution of carbonic anhydride and formation of oily drops (bromoform, according to Bandrowski) noticed by the aforesaid observers. The separation of the products of the reaction was effected by means of lead acetate; lead bromofumarate dissolves in 993 parts of water at 20°; lead dibromofumarate dissolves in 92 parts of water at 17°; lead dibromomaleate dissolves in 721 parts of water at 17°. When precipitated by the addition of lead acetate to the aqueous solution of the corresponding acid, the solubility of these salts is modified by the presence of the acetic acid. On the addition of a 10 per cent. solution of lead acetate, 1 part of bromofumaric acid in 350 parts of water will still give an immediate precipitate of aggregates of crystals; 1 part of dibromomaleic acid in 400 of water gives an immediate precipitate of specifically light needles; 1 part of bromomaleic acid in 400 parts of water gives an amorphous precipitate, whilst 1 part of dibromofumaric acid in 10 parts of water gives no precipitate even after several days.

The results of six experiments, in which mixtures of 1 gram of acetylenedicarboxylic acid and 1.4 gram of bromine with varying quantities of water were exposed to sunshine, bright diffused daylight, and dull diffused daylight, show that even in the presence of hydrobromic acid some 70 per cent. of the product consists of dibromofumaric acid and some 30 per cent. of dibromomaleic acid. The bromine content of the latter indicated that it was very nearly free from bromomaleic and bromofumaric acids, which might accompany it by the lead acetate precipitation method. The melting point of dibromofumaric acid is 227°.

To prove that Wislicenus is wrong in supposing that bromomaleic acid is the first product of the reaction, and that this is subsequently converted into bromofumaric acid by the hydrogen bromide formed by secondary reactions, the author submitted both acetylenedicarboxylic and bromomaleic acids to the action of hydrobromic acid under similar conditions, at the ordinary temperature, with the result that whilst much bromofumaric acid was formed from the acetylenedi-

carboxylic acid, the bromomaleïc acid remained unchanged. If Wislicenus' views be correct, tribromosuccinic acid should yield dibromofumaric acid by the elimination of hydrogen bromide, but when this is effected by the careful addition of aqueous potassium hydroxide to a well-cooled solution of the acid, much dibromomaleïc acid is produced, but practically no dibromofumaric acid.

Ethyl acetylenedicarboxylate, $C_2(COOEt)_2$ (compare Abstr., 1888, 1058), is a colourless liquid which boils with decomposition under the ordinary pressure, but distils without decomposition at 120—121° under 20 mm. pressure. It has a tear-exciting odour.

This salt was dissolved in varying quantities of carbon tetrachloride; the solutions were cooled to -17° , exposed to sunlight, and the calculated quantity of bromine, also dissolved in carbon tetrachloride, was gradually added to them. The reaction is one of the most facile in organic chemistry; only traces of hydrogen bromide are formed, showing the absence of secondary reactions. Three experiments gave, respectively, 74.9, 74.3, and 72.9 per cent. of ethyl dibromofumarate, contaminated with only very little bromofumarate and bromomaleate, and 25.1, 25.7, and 27.1 per cent. of ethyl dibromomaleate.

Ethyl dibromofumarate, $C_2Br_2(COOEt)_2$, forms large, colourless, lustrous prisms with oblique terminal planes; it melts at 67—68°, and is insoluble in water, but soluble in cold chloroform, benzene, acetone, and hot light petroleum. *Ethyl dibromomaleate* is a colourless oil which boils at 162—164° (20 mm.).

When an ethereal solution of ethyl dibromofumarate is heated with zinc in a sealed tube at 60—70°, a good yield of ethyl acetylenedicarboxylate is obtained. This reaction ought not to occur, according to the Van't Hoff-Wislicenus hypothesis (compare Abstr., 1891, 1184; 1888, 1147).
A. G. B.

Comparison of Experimental Results with the Theoretical Conclusions of the Van't Hoff-Wislicenus Hypothesis. By A. MICHAEL (*J. pr. Chem.* [2], 46, 400—424 and 424—427).—The experimental results referred to are those which have been recently published by Michael and his pupils, and a few earlier results obtained by others. A table showing 46 reactions, the results which these should give according to the Van't Hoff-Wislicenus hypothesis, the actual results, and references to the publications in which the experiments are detailed, are given.
A. G. B.

Synthesis of Isomalic acid. By K. BRUNNER (*Monatsh.*, 13, 834—839).—Hübner (*Annalen*, 120, 334; 124, 318) and Kleemann (Abstr., 1885, 505) both state that diacetyl cyanide, when treated with hydrochloric acid, is converted into hydrocyanic and acetic acids. The author finds that when it is treated at 0° with a solution of hydrogen chloride saturated at 0°, and after 24 hours the mixture is diluted with water, and the whole digested for some hours, isomalic and acetic acids are produced. The isomalic acid is identical with that described by Schmöger (Abstr., 1879, 618; 1882, 40). An improved method of preparing diacetyl cyanide is described.

L. T. T.

Homologues of Malic acid. By A. MICHAEL and G. TISSOT (*J. pr. Chem.* [2], 46, 285—304; compare Abstr., 1891, 1455).—To prepare β -hydroxypyrotartaric acid, potassium cyanide is mixed with ethyl acetoacetate in ethereal solution, and treated with hydrochloric acid. After two weeks, the ethereal layer is evaporated, and the residue digested with hydrochloric acid for 6—8 hours, and again dried. The acid is extracted from this residue by dry ethyl acetate. It is indistinguishable from citramalic acid, both in its own physical properties and those of its salts. The *ammonium* salt forms microscopic, hygroscopic prisms, melts at 145° , and decomposes at 155 — 160° . The silver salt crystallises in needles, and is anhydrous (compare Morris, *Trans.*, 1880, 10). When the acid is heated a little above its melting point, it is converted into citraconic anhydride and water. Morawski's citramalic acid was found to be identical with the acid just described. The identity of the two acids throws doubt on Morawski's statement that hydrochloroxycitraconic acid yields citramalic acid when reduced (this *Journal*, 1875, 1254); his experiment was therefore repeated, zinc being used as the reducing agent. The *methylmalic acid* obtained crystallises from ethyl acetate in white prisms, and melts at 123° (compare Wislicenus, Abstr., 1892, 589); its *calcium* salt (with 3 mols. H_2O), *lead* salt (with 1 mol. H_2O), and *zinc* salt are described.

$\alpha\beta$ -*Dimethylmalic acid* was prepared by substituting methyl ethyl-acetoacetate for ethyl acetoacetate in the prescription for preparing β -hydroxypyrotartaric acid. It crystallises in small, colourless prisms, melts at 143° , is very slightly hygroscopic, and dissolves in most solvents except light petroleum. The *silver* (with $\frac{1}{2}$ mol. H_2O), *barium* (with 2 mols. H_2O), and *calcium* (with $4\frac{1}{2}$ mols. H_2O) salts have been obtained. When the acid is heated at 175° , it yields dimethylmaleic anhydride (m. p. 96°).

$\alpha\beta$ -*Hydroxymethylethylsuccinic acid* (symmetrical ethylmethylmalic acid, Abstr., 1891, 1455) melts at 131.5 — 132° ; the *ammonium* salt melts at 179° ; the *silver* and *zinc* (with 4 mols. H_2O) salts were also prepared. The anhydride obtained by heating it, boils at 236 — 237° at ordinary pressure (not 226° , *loc. cit.*); the ammonium salt of the corresponding acid melts at 112° .

The behaviour of ethyl acetosuccinate with hydrocyanic acid is still being investigated (compare *loc. cit.*). A. G. B.

Ethyl Oxalacetate. By W. WISLICENUS and A. JENSEN (*Ber.*, 25, 3448—3456).—Ethyl oxalacetate reacts with aldehydes in the same manner as does ethyl acetoacetate (Claisen and Matthews, *Annalen*, 218, 270). When a mixture of ethyl oxalacetate and benzaldehyde in molecular proportion is saturated in the cold with dry hydrogen chloride, and allowed to remain in a closed vessel for some days, *ethyl benzylidenoxalacetic acid*, having most probably the constitution $\text{COOH}\cdot\text{CO}(\text{CHPh})\cdot\text{COOEt}$, separates. It crystallises in small, lustrous, felted needles, melts at 104 — 105° , distils partially undecomposed, under diminished pressure, and is readily soluble in alcohol and ether, but only sparingly in hot water. The *copper* salt, $\text{C}_{13}\text{H}_{11}\text{O}_5\text{Cu}$, is obtained as an oil, but subsequently solidifies; it crystallises from methyl alcohol

with 2 mols. of the solvent in rhombic plates melting at 117—119°. After eliminating the methyl alcohol by heating the salt in a toluene bath, it melts at 145° with decomposition. When the salt is distilled under diminished pressure, ethyl cinnamate passes over. The *phenylhydrazine* salt, $C_{19}H_{20}N_2O_5$, is formed by adding the calculated quantity of phenylhydrazine to a solution of the acid ethyl salt in dilute alcohol. It crystallises in stellate groups of needles, melts at 99°, and is readily converted into the *osazone* with the loss of water.

The *monhydrazone* of dihydroxytartaric acid, $C_{14}H_{16}N_2O_5$, is obtained in accordance with R. Meyer's views (*Annalen*, **247**, 190) when ethyl oxalacetate, dissolved in aqueous potash, is treated with diazobenzene chloride; it forms long, yellow needles, melts at 72—73° with the evolution of gas, and is readily soluble in ether, chloroform, and aqueous alkalis, but insoluble in water. Its yellow solution in concentrated sulphuric acid is coloured deep violet by potassium dichromate. If the compound is dissolved in alcohol and treated with phenylhydrazine, the *osazone* obtained by Anschütz and Geldermann (*Abstr.*, 1891, 725) from ethyl dihydroxytartrate is formed, and when this is boiled with glacial acetic acid, it is converted into ethyl phenylhydrazonketophenylpyrazolonecarboxylate (Wislicenus and Scheidt, *Abstr.*, 1892, 458).

When an alkaline solution of diazobenzene chloride (2 mols.) is quickly added to one of ethyl oxalacetate (1 mol.), ethyl formazylcarboxylate, described by v. Pechmann (this vol., i, 82), and also by Bamberger and Wheelwright (*ibid.*, 84), is obtained. It agrees with the descriptions of these chemists, and when rapidly heated, melts at 113—114°; it also gives, on hydrolysis with alcoholic potash, an acid identical with that of v. Pechmann and Bamberger (*loc. cit.*).

A. R. L.

Optical Isomerides of d-Mannoheptonic acid, d-Mannoheptose, and Perseitol. By W. S. SMITH (*Annalen*, **272**, 182—190).—The compounds described below have been obtained from l-mannose by the same methods as those employed in preparing the corresponding compounds of the d-series (compare Fischer and Passmore, *Abstr.*, 1890, 1230); the inactive substances were obtained by combining the members of the two optically active series in the usual way, but in many cases it could not be ascertained with certainty whether these products are the true racemic modifications or simply mixtures.

l-Mannoheptonic acid was isolated in the form of its crystalline barium salt, $(C_7H_{13}O_8)_2Ba$. The *lactone*, $C_7H_{12}O_7$, separates from alcohol in crystals, melts at 153—155°, and has a specific rotatory power $[\alpha]_{D20} +75.15^\circ$ in aqueous solution. The *hydrazide*, $C_7H_{13}O_7 \cdot N_2H_2Ph$, separates from hot water in crystals, and melts at about 220° with decomposition when quickly heated.

i-Mannoheptonic acid was obtained in the form of the *lactone*, $C_7H_{12}O_7$; this substance crystallises in small needles, melts at about 85°, has a sweet taste, and is rather more sparingly soluble in water than the two active lactones. The *calcium* salt, $(C_7H_{13}O_8)_2Ca + H_2O$, prepared from the *lactone*, crystallises from water in small, quadratic prisms, and loses its water at 110°. The *hydrazide*, $C_{13}H_{20}N_2O_7$, crys-

tallises from water in microscopic needles, and melts at 225° with decomposition.

l.-Mannoheptose is a colourless, deliquescent powder, and seems not to ferment with yeast. Its *hydrazone* crystallises from hot water in slender, colourless needles melting at about 196° with decomposition. Its *osazone*, $C_7H_{12}O_5(N_2HPh)_2$, crystallises from hot alcohol in slender needles and melts at about 203° with decomposition.

i.-Mannoheptose is a colourless syrup, only sparingly soluble in alcohol, and does not ferment with yeast. The *hydrazone* melts at $175-177^{\circ}$ with decomposition. The *osazone*, $C_7H_{12}O_5(N_2HPh)_2$, crystallises in yellow needles, and melts at about 210° with decomposition.

l.-Mannoheptitol, $C_7H_{16}O_7$, separates from hot methyl alcohol and from hot water in crystals, and melts at 187° (corr.).

i.-Mannoheptitol, $C_7H_{16}O_7$, crystallises from water in microscopic plates, and melts at 203° (corr.).

F. S. K.

Derivatives of d.-Mannoheptonic acid. By G. HARTMANN (*Annalen*, 272, 190—197).—Fischer has shown that two stereoisomeric acids are usually formed by the hydrolysis of the product of the combination of a sugar with hydrogen cyanide; the author's experiments prove that the acid obtained in this way from d.-mannose (Abstr., 1890, 1230), in quantities amounting to 87.4 per cent. of the theoretical, is not a mixture, and that the stereochemical isomeride is not produced in the reaction in question.

Calcium d.-mannoheptonate, $(C_7H_{13}O_8)_2Ca$, is soluble in about 30 parts of hot water, from which it crystallises in slender needles; the *strontium* salt, $(C_7H_{13}O_8)_2Sr$, is a semi-crystalline compound, much more readily soluble in water. The *cadmium* salt, $(C_7H_{13}O_8)_2Cd$, crystallises in well-defined needles, and is soluble in about 100 parts of boiling water.

Attempts to resolve d.-mannoheptonic acid into two stereochemical isomerides by means of its strychnine and brucine salts were unsuccessful; the *brucine* salt, $C_7H_{11}O_8 \cdot C_{23}H_{26}N_2O_4$, separates from hot 90 per cent. alcohol in well-defined crystals, melts at 161° , and seems to contain water of crystallisation.

Pentahydroxypimelic acid, $COOH \cdot [CH \cdot OH]_5 \cdot COOH$, is formed when d.-mannoheptonic acid is oxidised with nitric acid of sp. gr. 1.2 at $45-50^{\circ}$; when purified by means of its calcium salt, it is obtained as a yellow syrup, very readily soluble in water and alcohol, the aqueous solution being lævo-rotatory. The *calcium* salt, $C_7H_{10}O_9Ca + 4H_2O$, separates from hot water in the form of a crystalline powder; it loses its water at 108° , and is only sparingly soluble in hot water. The *ethyl* salt, $C_{11}H_{20}O_9$, is formed when the acid is repeatedly evaporated with alcohol; it crystallises from hot alcohol in colourless needles, melts at 166° , and is readily soluble in water. The *dihydrazide*, $C_5H_{10}O_5(CO \cdot N_2H_2Ph)_2$, crystallises in yellowish plates, and melts at about 225° with decomposition when quickly heated.

F. S. K.

Lactosecarboxylic acid and Maltosecarboxylic acid. By O. REINBRECHT (*Annalen*, 272, 197—200).—*Lactosecarboxylic acid*,

$C_{12}H_{23}O_{11} \cdot COOH$, can be prepared by treating lactose with hydrogen cyanide under the usual conditions, and hydrolysing the product with barium hydroxide; it is a colourless, vitreous substance, has a sour taste, and does not reduce Fehling's solution. Its *calcium*, *strontium*, and *barium* salts are amorphous and readily soluble. When the acid is warmed with dilute mineral acids, it is decomposed into galactose and α -glucoheptonic acid.

Maltosecarboxylic acid, prepared from maltose in a similar manner, resembles the preceding compound; on hydrolysis with mineral acids, it is decomposed into glucose and α -glucoheptonic acid.

F. S. K.

Hydurilic acid. By C. MATIGNON (*Compt. rend.*, **115**, 955—958).—Hydurilic acid, $C_8H_6N_4O_2$, forms monopotassium and dipotassium salts (compare Baeyer, *Annalen*, **127**, 14). The heat of neutralisation with 2 mols. of potash is 21.8 Cal., but on adding a further quantity (up to 16 mols.), 4.2 Cal. more is liberated, thus pointing to a third very feeble acid function. The heat of neutralisation for the *monopotassium* salt (3 mols. potash) is +7.8 Cal., so that the heat of formation of the salt (calculated for solids throughout) is +32.0 Cal. The *dipotassium* salt, with $3H_2O$, absorbs 4.2 Cal. when dissolved in potash (2 mols.), so that the value of the second acid function is +21.7 Cal.

J. N. W.

Aromatic Iodochlorides, Iodosobenzene, and Iodoxybenzene. By C. WILLGERODT (*Ber.*, **25**, 3494—3502).—Iodochlorides are obtained by treating aromatic iodo-compounds dissolved in chloroform or carbon tetrachloride with chlorine (compare Abstr., 1886, 341).

Diiodobenzene tetrachloride, $C_6H_4I_2Cl_4$ or $C_6H_4(ICH_2)_2$, is a greenish-yellow powder, decomposes at 155—156°, and darkens on exposure to light and air.

Triiodobenzene hexachloride, $C_6H_3I_3Cl_6$ or $C_6H_3(ICH_2)_3$, decomposes at 145°.

Phenyl iodochloride, when exposed to damp air, becomes opaque, and decomposes with evolution of hydrogen chloride.

Orthiodophenol reacts with chlorine with evolution of hydrogen chloride, and, after a time, the liquid deposits a yellow, crystalline iodochloride, which soon decomposes with elimination of iodine.

Iodosobenzene, $C_6H_5 \cdot IO$, is obtained by treating phenyl iodochloride with an aqueous solution of potassium or sodium hydroxide. It is a yellow, amorphous compound, has a characteristic odour, explodes violently when heated to 210°, and yields phenyl iodochloride when treated with phosphorus pentachloride. It reacts explosively with aniline and picric acid, and oxidises formic acid to carbonic acid. With acids, it forms salts. The *acetate*, $IPh(OAc)_2$, crystallises in large, colourless prisms, melts at 156—157°, and is neutral to litmus. The benzene solution becomes acid on boiling. The *propionate* crystallises in colourless needles and prisms, and melts at 63—64°. The *normal butyrate* melts at 68—69°. The *hydrochloride* crystallises in long needles. The *nitrate*, $IPh(NO_3)_2$, obtained by dissolving iodosobenzene in dilute nitric acid, crystallises in large, greenish-yellow prisms, and decomposes at 105—106° with a feeble explosion.

Iodosobenzene also dissolves in hydrofluoric, fluosilicic, and sulphuric acids.

Iodoxybenzene, $C_6H_5 \cdot IO_2$, is obtained by heating iodosobenzene at $90-100^\circ$ in the air. It crystallises in white needles, explodes at $227-230^\circ$, and is neutral. It explodes when treated with phosphorus pentachloride or strong sulphuric acid. With aniline, it gives a blood-red coloration. With fuming nitric acid, it yields paranitriodobenzene (m. p. 165°).
E. C. R.

Hydrogenation of Benzene. By N. KIJNER (*J. Russ. Chem. Soc.*, 23, 20—26).—1 c.c. of pure benzene was sealed up in a tube with 25 c.c. of hydriodic acid of sp. gr. 1.96 and heated for 24 hours at 280° . The layer of hydrocarbon was separated, washed with a solution of alkali, distilled with steam, and dried with calcium chloride. 24 grams of the substance obtained in this way were fractionated, and yielded 18 grams distilling between 69° and 73° . The residue was again treated with fuming hydriodic acid, and the hydrocarbon from it began to boil at 71° , most of it passing over below 75° , but a small quantity of high boiling material remained, which only distilled above 170° . As this did not react with fuming nitric acid, it could only be a condensation product of fully hydrogenised benzene, and not of benzene itself. The sp. gr. of the chief fraction ($69-73^\circ$) was 0.7838 at 0° , indicating the presence of unchanged benzene. In order to remove this admixture, the following process was adopted:—

Triphenylmethane was melted and mixed with the liquid. On cooling, it crystallised out, taking along with it a large proportion of the benzene. The liquid was poured off and again treated in the same way. On fractionation, it now passed over almost entirely between 68° and 70° at 751 mm., its sp. gr. being 0.7609 at $0^\circ/0^\circ$ and 0.7423 at $19.5^\circ/0^\circ$. It still reacted feebly at 0° with fuming nitric acid, after treatment with which it was again dried and distilled. It now came over between 69° and 71° at 761 mm., and had the sp. gr. 0.7473 at $0^\circ/0^\circ$. The numbers obtained on analysis, agreed well with the formula C_6H_{12} , although it is probable that the substance was not quite free from hexane.

Fuming sulphuric acid, if in great excess, dissolves hexahydrobenzene with slight development of heat, the acid becoming brown and giving off sulphurous anhydride.

Fuming nitric acid at 0° scarcely acts on hexahydrobenzene, but, if the mixture is not cooled, the hydrocarbon dissolves with disengagement of heat. No oil separates when the mixture is poured into water, and no smell of nitrobenzene can be detected. A mixture of nitric and sulphuric acids is also without nitrating effect.

Excess of bromine in presence of a small quantity of aluminium bromide gives with hexahydrobenzene, a crystalline compound, which, after recrystallisation from benzene, melts at $124-125^\circ$. The compound cannot, therefore, be hexabromobenzene, as Konovaloff's experiments would lead one to expect (*J. Russ. Chem. Soc.*, 11, 146).

J. W.

Sandmeyer's Reaction and Preparation of Orthochlorotoluene. By H. ERDMANN (*Annalen*, 272, 141—147; compare Arm-

strong and Wynne, *Proc.*, 1892, 199).—In discussing Sandmeyer's reaction, the author points out that it is the formation of phenols and of azo-compounds which diminishes the yield when the conditions are not suitably chosen. The production of a phenol is due to the decomposition of the diazo-compound before it has been converted into the cuprous chloride compound, this taking place more especially when the amido-compound is diazotised in too concentrated solution, or at too high a temperature, or without stirring well; also when the solution of the diazo-compound is added too slowly to the boiling cuprous chloride solution.

The normal decomposition of the diazo-cuprous chloride compound takes place rapidly and smoothly only above a certain temperature, which is different for each compound; these temperatures are about 0° , about 27° , about $30-40^{\circ}$, and about $40-50^{\circ}$ in the case of the cuprous chloride derivatives of diazobenzene, orthodiazotoluene, para-diazotoluene, and paradiazochlorobenzaldehyde respectively. Below these particular temperatures, the evolution of nitrogen takes place too slowly, and is incomplete, part of the diazo-cuprous chloride compound being reduced to an azo-compound by the liberated cuprous chloride, which is then present in excess; the yield of pure azo-compound may sometimes amount to more than 10 per cent. of the base employed.

When the diazo-compound is very readily decomposed, as is that of orthotoluidine, for example, the amido-base should be diazotised in very dilute, well-cooled solution, and the product decomposed with cuprous chloride at a low temperature; under these conditions, the yield of pure orthochlorotoluene is 70 per cent. of the theoretical.

F. S. K.

Heptanaphthene from Caucasian Naphtha. By E. SPINDLER (*J. Russ. Chem. Soc.*, **23**, 40—44).—Milkoffsky isolated from Caucasian naphtha a hydrocarbon, C_7H_{14} , boiling at $100-101^{\circ}$, and having the properties of a saturated hydrocarbon. From this, he obtained a chlorinated compound, which he did not investigate further. The chloro-derivative boils at $157-159^{\circ}$, and has the composition $C_7H_{13}Cl$. If impure, it gives off small quantities of hydrogen chloride on being distilled, but the pure substance distils unchanged. Its sp. gr. at $0^{\circ}/0^{\circ}$ is 0.9769; at $20^{\circ}/0^{\circ}$, 0.9589. From the chloride, the author prepared a heptanaphthylene, by heating 1 part of it with $1\frac{1}{2}$ parts of potassium acetate and a little strong acetic acid in a sealed tube at 210° for 11 hours. The contents of the tube were neutralised with alkali and distilled with steam; a layer lighter than water separated from the distillate, and this layer was washed, dried, and distilled. The chief portion boiled at $102-104^{\circ}$, a few drops between 110° and 180° , and about a fourth of the whole between 180° and 190° . The portion boiling between 102° and 104° , when analysed, yielded numbers agreeing with the formula C_7H_{12} . The sp. gr. of this heptanaphthylene is 0.8085 at $0^{\circ}/0^{\circ}$, and 0.7910 at $20^{\circ}/0^{\circ}$. It combines with hydrogen bromide at the ordinary temperature and at 100° , but not energetically, and a portion of the hydrocarbon always remains unattacked.

Heptanaphthene, when dropped into 12 times its weight of bromine in presence of aluminium bromide, reacts energetically at first, but the reaction soon moderates, and hydrogen bromide at last comes off only very slowly. A crystalline substance is formed, which, when freed from a slight admixture of an oil and recrystallised from benzene, melts at $282-283^{\circ}$. At a higher temperature, it volatilises, forming white needles in the cooler portions of the tube. Its composition corresponds with the formula $C_7H_5Br_5$, and the melting point indicates that it is pentabromotoluene.

It would thus appear that the heptanaphthene from Caucasian petroleum is hexahydrotolnene, the boiling point of the latter being, however, 97° , instead of $100-101^{\circ}$. J. W.

Hydrolysis of Phenolic Ethers and of Ethereal Salts by means of Aluminium Chloride. By C. HARTMANN and L. GATTERMANN (*Ber.*, **25**, 3531—3534).—Phenolic ethers are readily hydrolysed by the action of aluminium chloride; the method is also applicable to nitro- and ketonic compounds, which are reduced on treatment with hydriodic acid.

Methoxybenzene, ethoxybenzene, and isobutoxybenzene, respectively, are hydrolysed by heating for three hours at 120° with 1.5 parts of aluminium chloride.

With orthonitro-methoxy- or ethoxy-benzene, the reaction proceeds more energetically; the phenol (1 part) should be dissolved in an equal weight of carbon bisulphide, and treated with aluminium chloride (1 part). The yield is 90 per cent. of the theory.

Orthohydroxymethoxybenzene and orthomethoxyhydroxytoluene [1:3:4], on treatment with aluminium chloride at 210° , give orthodihydroxybenzene and orthodihydroxytoluene respectively; the yield is 70 per cent. of the theoretical.

Parahydroxyacetophenone is obtained by heating aluminium chloride with paracetylmethoxybenzene at 140° , or with paracetylethoxybenzene at 180° ; the yield is 70 per cent.

Parahydroxybenzophenone and α -hydroxyacetophthalene may be prepared in a similar manner from aluminium chloride and benzoylmethoxybenzene, or α -ethoxyacetophthalene, by heating for $1\frac{1}{2}$ hours at $200-210^{\circ}$.

Many ethereal salts are also hydrolysed by the action of aluminium chloride; the authors have experimented with the ethyl salts of the following acids: acetic, succinic, phthalic, cinnamic, and paranitrocinnamic, and also with methyl salicylate. J. B. T.

Propylamidophenol from Camphor. By P. CAZENEUVE (*Compt. rend.*, **115**, 825—827).—The nitroketone, $NO_2 \cdot C_9H_{11}O$, obtained by the action of nitric acid on the sulphone derived from monochlorocamphor (*Abstr.*, 1892, 999), when treated with tin and hydrochloric acid, yields an amidophenol, the ketonic group, $-CH_2 \cdot CO-$, being converted into a phenolic group, $-C(OH) : CH-$, by intramolecular migration at the time that the nitro-group is reduced. The product has the composition $NH_2 \cdot C_6H_3Pr \cdot OH$, and is purified by precipitation by ammonia from the solution of its hydrochloride, and repeated

recrystallisation from benzene. The base forms lamellar crystals, composed of slender, microscopic needles, which melt at 122° with slight decomposition, and distil at 260° partially without decomposition; it is insoluble in water, but dissolves in alcohol, ether, and benzene, and is also soluble in acids and alkalis. The alkaline solutions oxidise very rapidly when exposed to air, and become brownish-yellow. The alcoholic solution of the base gives a wine-red coloration with ferric chloride; the aqueous solution of the hydrochloride gives an intense red coloration and a precipitate with the same reagent. The *acetyl* derivative is insoluble in alkalis, and gives no coloration with ferric chloride. The base forms a slightly soluble picrate, which crystallises in beautiful needles; a slightly soluble ferrocyanide, which is crystallisable, but slowly decomposes; and a maroon-coloured insoluble platinochloride, which is very readily oxidised. Hydroxylamine and phenylhydrazine are without action, but when the compound is heated with zinc-dust in a current of hydrogen, it yields a hydrocarbon, C_9H_{12} , which boils at 150 — 156° . Cumene boils at 151° , and propylbenzene at 157° .

When the base is treated with concentrated sulphuric acid and alcohol, and the theoretical quantity of an aqueous solution of an alkaline nitrite is added, a phenol is obtained, and hence it is clear that the phenol group pre-exists in the base. A solution of nitric acid in sulphuric acid gives a bright red coloration with solutions of the base.

From these results, it would seem that the new base is a propylamidophenol [$NH_2 : OH : Pr = 1 : 3 : 4$], and it follows that the fundamental nucleus of camphor is really paracymene, as the other reactions of camphor indicate.

C. H. B.

Action of Thiocarbimides on Aromatic Hydrocarbons.

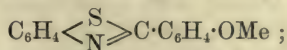
By A. FRIEDMANN and L. GATTERMANN (*Ber.*, 25, 3525—3528).—Lenckart has shown (Abstr., 1885, 773, 1224) that phenyl cyanate unites with aromatic hydrocarbons in presence of aluminium chloride with formation of anilides, phenyl cyanate and benzene giving benzanilide, $NHPh \cdot CPh$; he was unable, however, to carry out a similar reaction with the thiocarbimides, and the author had likewise since attempted the same reaction without success. A renewed attempt, in which pure aluminium chloride, prepared from aluminium and hydrogen chloride, was employed, has brought about the desired result.

To carry out the reaction, a mixture of phenylthiocarbimide and benzene is heated on the water-bath with pure aluminium chloride for $1\frac{1}{2}$ hours, and then allowed to remain 24 hours, after which water is carefully added, and the mixture steam distilled. The product of the reaction separates from the residue on cooling, and consists of a mixture of two compounds, which can be separated by treatment with dilute alkali. The solution, when acidified, yields thiobenzanilide, $NHPh \cdot CPh$; whilst the residue, after treatment with alkali, has the composition $C_{14}H_{10}N_2S_3$, and can also be formed by the action of aluminium chloride on phenylthiocarbimide alone, phenylcarbamide being simultaneously produced; it crystallises from alcohol in pale-yellow,

lustrous needles melting at 154° . Its constitution is not yet exactly determined.

With aluminium chloride, phenylthiocarbimide and toluene yield thiotoluylanilide only, $\text{NHPh}\cdot\text{CS}\cdot\text{C}_6\text{H}_4\text{Me}$, which separates from alcohol in long, yellow needles melting at $140\text{--}141^{\circ}$; paratolylthiocarbimide and toluene yield, chiefly, the thioanilide, which melts at $165\text{--}166^{\circ}$; in the absence of toluene, a substance insoluble in alkali is formed, which separates from acetone in well-developed sulphur-yellow crystals, and melts at $175\text{--}176^{\circ}$. H. G. C.

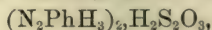
Action of Phenol Ethers on Thiocarbimides. By K. TUST and L. GATTERMANN (*Ber.*, **25**, 3528—3530).—Phenol ethers, like hydrocarbons, react with thiocarbimides in presence of pure aluminium chloride, but the action proceeds much more smoothly. Anisoil and phenylthiocarbimide yield the *thioanilide* of *anisic acid*, $\text{NHPh}\cdot\text{CS}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, which separates from alcohol in yellow crystals melting at $153\text{--}154^{\circ}$. It readily undergoes oxidation on treatment with potassium ferricyanide, forming the compound



this crystallises from acetic acid in colourless needles, and melts at $134\text{--}135^{\circ}$. Phenetoil and phenylthiocarbimide yield the corresponding thioanilide, $\text{NHPh}\cdot\text{CS}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, which forms yellow needles melting at 143° , and on oxidation with ferricyanide is converted into the compound $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{S} \\ \text{N} \end{smallmatrix} \geq \text{C}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$. α -Naphthyl ethyl ether and phenylthiocarbimide yield the thioanilide, $\text{NHPh}\cdot\text{CS}\cdot\text{C}_{10}\text{H}_7\cdot\text{OEt}$, which crystallises from acetic acid in yellow needles, and melts at $199\text{--}200^{\circ}$. Other thioanilides of different phenol ethers have also been prepared by the same reaction. H. G. C.

Aromatic Diazo-compounds. By H. v. PECHMANN (*Ber.*, **25**, 3505).—The author believes that paradiazotoluene exists in alkaline solution as a nitrosamine, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{NO}$, for when the alkaline solution is treated with benzoic chloride, a compound is obtained which is probably nitrosobenzotoluidide, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}(\text{NO})\cdot\text{COPh}$. This crystallises from acetone in colourless needles, is very unstable, explodes when heated, gives Liebermann's reaction, and when reduced with zinc-dust and acetic acid yields parabenztoluidide (m. p. $157\text{--}158^{\circ}$). E. C. R.

Salts and Derivatives of Phenylhydrazine. By B. THIEME (*Annalen*, **272**, 209—213).—*Phenylhydrazine thiosulphate*,



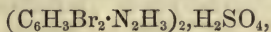
crystallises in colourless plates, melts at about 113° with decomposition when quickly heated, and is insoluble in ether; when heated at $120\text{--}130^{\circ}$ for a long time, it is completely decomposed, yielding nitrogen, ammonia, hydrogen sulphide, benzene, aniline, thiophenol, and diphenyl sulphide. The *sulphite*, $(\text{N}_2\text{PhH}_3)_2\cdot\text{H}_2\text{SO}_3$, crystallises in small, colourless plates, and melts at about 94° with decomposition.

when quickly heated. The nitrate, $\text{N}_2\text{PhH}_3\cdot\text{HNO}_3$, melts at about 145° with decomposition. The *phosphate*, $(\text{N}_2\text{PhH}_3)_2\cdot\text{H}_3\text{PO}_4$, prepared by mixing concentrated solutions of disodium hydrogen phosphate and phenylhydrazine acetate, forms small plates, and melts at about 155° with decomposition. The *hydrofluoride*, $\text{N}_2\text{PhH}_3\cdot\text{HF}$, is formed when hydrogen fluoride is passed into an alcoholic solution of excess of the base; it melts at about $166\text{--}167^\circ$ with decomposition. The *acid hydrofluoride*, $\text{N}_2\text{PhH}_3\cdot 2\text{HF}$, is produced when the normal salt is treated with alcohol; it forms slender needles, sublimes with partial decomposition, and is insoluble in ether.

A compound, which seems to have the composition $(\text{N}_2\text{PhH}_3)_2\cdot\text{P}_2\text{O}_5$, is formed when an ethereal solution of phenylhydrazine is added to phosphoric anhydride; it melts at $242\text{--}248^\circ$ with decomposition.

F. S. K.

Bromination of Phenylhydrazine. By P. MEYER (*Annalen*, 272, 214—220).—*Orthodibromophenylhydrazine* [$\text{N}_2\text{H}_3 : \text{Br}_2 = 1 : 3 : 4$] can be prepared by brominating acetonephenylhydrazone in chloroform solution and decomposing, with soda, the hydrobromide obtained in this way; it crystallises from alcohol in moss-like needles, melts at 104° , and turns brown on exposure to the air. The *hydrochloride*, $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{N}_2\text{H}_3\cdot\text{HCl}$, crystallises in lustrous needles, melting just above 200° with decomposition. The *sulphate*,



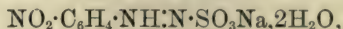
is readily soluble in water, and crystallises in lustrous needles. The *nitrate* forms colourless needles, and melts at about 163° with decomposition. The *picrate*, $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{N}_2\text{H}_3\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, melts at about 132° with decomposition. The *oxalate*, $(\text{C}_6\text{H}_3\text{Br}_2\cdot\text{N}_2\text{H}_3)_2\cdot\text{C}_2\text{H}_2\text{O}_4$, crystallises in colourless plates melting at about 174° with decomposition. The *acetyl* derivative, $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{N}_2\text{H}_2\text{Ac}$, separates from hot alcohol in long, colourless needles, and melts at about $162\text{--}163^\circ$ with decomposition. The *benzylidene* derivative, $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{N}_2\text{H}:\text{CHPh}$, crystallises from light petroleum in colourless needles, and melts at 123° . When orthodibromophenylhydrazine is reduced with zinc-dust and hydrochloric acid, it is converted into parabromaniline, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$.

Metadibromophenylhydrazine [$\text{N}_2\text{H}_3 : \text{Br}_2 = 1 : 2 : 4$], prepared from metadibromaniline in the usual manner, crystallises in colourless, moss-like needles, melts at 91° , and decomposes at about 178° ; the *hydrochloride* crystallises in long needles. The *acetyl* derivative, $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{N}_2\text{H}_2\text{Ac}$, separates from alcohol in colourless prisms melting at 146° . When metadibromophenylhydrazine is reduced with zinc-dust and hydrochloric acid, it is converted into parabromaniline; the last-named compound is also obtained from metadibromaniline under the same conditions.

F. S. K.

Paranitrophenylhydrazine. By A. PURGOTTI (*Real. Accad. Linc.*, 7, ii, 266—270).—A mixture of paranitraniline, hydrochloric acid, and water is diazotised with a solution of sodium nitrite. The product is slowly poured into sodium hydrogen sulphite solution, cooled with ice, and subsequently heated on the water-bath at 70° , with occasional addition of sodium hydrogen sulphite, so that the solution always

has a strong odour of sulphurous anhydride. The reddish precipitate formed soon coagulates and is filtered off; after further evaporation of the filtrate, *sodium paranitrophenylhydrazinesulphonate*,



separates. It forms minute, yellow crystals, which begin to decompose at 115–120°, and deflagrate on ignition; it is readily soluble in water, sparingly so in alcohol, and rapidly reduces silver nitrate and Fehling's solution. The *barium* salt forms yellowish, spherical, acicular aggregates, containing 1 mol. H_2O ; it is sparingly soluble in hot water, decomposes above 180°, and is a strong reducing agent.

On heating the sodium salt with hydrochloric acid (sp. gr. 1.19), and cooling the solution, *paranitrophenylhydrazine*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{H}_3$, HCl , separates; it forms small, reddish crystals, and is sparingly soluble in alcohol. Its aqueous solution slowly decomposes on exposure to the air.

Paranitrophenylhydrazine is obtained by heating the aqueous solution of the hydrochloride with sodium acetate, the precipitate being crystallised from boiling alcohol. It forms small, brown scales or needles, and melts at 157° with evolution of gas; it is very soluble in hot alcohol, but only sparingly in cold alcohol or water, and insoluble in benzene. It reduces silver nitrate or Fehling's solution, and on boiling with benzaldehyde in alcoholic solution, yields reddish crystals, which melt at 190°; this substance is now under examination.

W. J. P.

Synthesis of Formazyl Compounds by the Action of Diazobenzene on Hydrazones. By W. WISLICENUS (*Ber.*, 25, 3456–3458; compare this vol., i, 82).—Formazylphenyl separates when diazobenzene chloride is added to benzylidenehydrazone and sodium ethoxide; it melts at 167–168°, whereas v. Pechmann states that the melting point is “about 175°”; the disparity in the values may, however, be due to a difference in the manner of heating.

Diazobenzene chloride and glyoxylic hydrazone react in a similar way, forming formazylazobenzene, which v. Pechmann has obtained from mesoxalic hydrazone, and Bamberger from ethyl acetoacetate.

A. R. L.

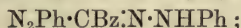
Action of Diazobenzene on β -Ketonic acids. By E. BAMBERGER (*Ber.*, 25, 3547–3555; compare this vol., i, 84, and v. Pechmann, this vol., i, 82).—v. Pechmann's work on the interaction of diazobenzene and hydrazones of the formula $\text{NPh} \cdot \text{N} \cdot \text{CXY}$ has led him to the conclusion that, when X and Y represent hydrogen, carbonyl, carbethoxyl, or an acid radicle, they are eliminated in the form of their hydroxyl compounds, and are replaced by the group $\text{NPh} \cdot \text{N}$. Whilst agreeing substantially with v. Pechmann's statement, the author finds no evidence to show that the carbethoxy- and benzoyl groups can be displaced by the diazobenzene radicle.

Ethyl acetoacetate, when treated with diazobenzene in alkaline solution, yields practically pure ethyl formazylcarboxylate, $\text{NPh} \cdot \text{N} \cdot \text{C}(\text{N} \cdot \text{NPh}) \cdot \text{COOEt}$.

By the action of acetoacetic acid on diazobenzene, pure phenylazoformazyl, $C(N:NPh)_2:N \cdot NPh$, is formed.

Ethyl formazylcarboxylate is not acted on by diazobenzene in alkaline solution at 0° , but formazylcarboxylic acid, under the same conditions, is converted into phenylazoformazyl.

Ethyl benzoylacetate, on treatment with diazobenzene at 0° , yields ethyl phenylhydrazonebenzoylformate, $N_2HPh:CBz:COOEt$. Benzoylacetic acid and diazobenzene give formazyl phenyl ketone,

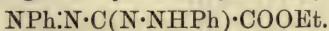


by the further action of diazobenzene on this substance, phenylazoformazyl appears to be formed in very small quantity; the greater part of the ketone is, however, recovered unchanged.

Ethyl acetoacetate and acetoacetic acid yield at least five compounds with diazobenzene, according to the experimental conditions; they are shown in the following table, together with other compounds formed from diazobenzene and various acids and ethereal salts. It will be seen that the hydrazone radicle is not always eliminated by the action of diazobenzene:—

Ethyl acetoacetate (1 mol.) and diazobenzene (1 mol.) give ethyl benzeneazoacetate, $COOEt:CAC:N \cdot NPh$.

Ethyl acetoacetate (1 mol.) and diazobenzene (2 or 3 mols.) in alkaline solution give ethyl formazylcarboxylate,



Acetoacetic acid (1 mol.) and diazobenzene (1 mol.) in acetic acid solution give pyruvic aldehyde hydrazone, $CHAc:N \cdot NPh$, and formazyl methyl ketone, $N_2Ph:CAc:N \cdot NPh$.

Acetoacetic acid (1 mol.) and diazobenzene (2 mols.) in alkaline carbonate solution give formazyl methyl ketone.

Acetoacetic acid (1 mol.) and diazobenzene (3 mols.) in alkaline solution give phenylazoformazyl, $NHPh:N \cdot C(N:NPh)_2$.

Ethyl alkyl acetoacetate (1 mol.) and diazobenzene (1 mol.) give ethyl pyruvate hydrazone, $NHPh:N:CMe \cdot COOEt$.

Alkylacetoacetic acid (1 mol.) and diazobenzene (1 mol.) give diacetylphenylhydrazone, $NHPh:N:CMeAc$.

Alkylacetoacetic acid (1 mol.) and diazobenzene (2 mols.) give methylformazyl, $NHPh:N:CMe:N \cdot NPh$.

Ethyl benzoylacetate (1 mol.) and diazobenzene (1 or 3 mols.) give ethyl benzoylglyoxalate hydrazone, $NHPh:N:CBz:COOEt$.

Benzoylacetic acid (1 mol.) and diazobenzene (1 mol.) give phenylglyoxalic hydrazone, $NHPh:N:CHBz$, and formazyl phenyl ketone, $NHPh:N:CBz:N \cdot NPh$.

Benzoylacetic acid (1 mol.) and diazobenzene (2 or 3 mols.) give formazyl phenyl ketone.

Ethyl hydrogen malonate hydrazone (1 mol.) and diazobenzene (1 mol.) give ethyl formazylcarboxylate, $NHPh:N \cdot C(N:NPh) \cdot COOEt$.

J. B. T.

Formazyl Methyl Ketone. By E. BAMBERGER and J. LORENZEN (*Ber.*, 25, 3539—3547; compare this vol., i, 84).—The constitution of formazyl methyl ketone is shown by its formation from benzeneazo-

acetoacetic acid and diazobenzene, whilst by the action of diazobenzene in presence of an alkali on the ketone, acetic acid and phenylazoformazyl are produced.

β -Phenotriazyl α -methyl ketone, $C_6H_4 < \begin{smallmatrix} N:N \\ N:C^{Ac} \end{smallmatrix}$, is obtained by the action of mineral acids on formazyl methyl ketone; it crystallises in yellow, glistening needles, melts at $121.5-122.5^\circ$, has feebly basic properties, and is readily soluble in mineral acids, alcohol, and chloroform, insoluble in water and light petroleum. The *phenylhydrazone*, $C_7H_5N_3 \cdot CMe \cdot N \cdot NPh$, resembles azobenzene in appearance, and crystallises in flat, brick-red, lustrous needles melting at 202° with previous softening; with sulphuric acid, a greenish-brown coloration is produced, changing to deep blue on the addition of potassium dichromate or ferric chloride.

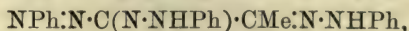
On reduction with stannous chloride in acid solution, phenotriazyl methyl ketone yields a compound which crystallises in prisms, melts at 165° , and is being further investigated.

By the action of ammonium sulphide on formazyl methyl ketone in alcoholic solution, a reduction product is obtained which crystallises in flat, yellow, lustrous needles, melts at 183° , and may be recrystallised from water. The substance is probably represented by the

formula $C_6H_4 < \begin{smallmatrix} NH:NH \\ N=C \end{smallmatrix} \cdot CHMe \cdot OH$; on treatment with acetic anhydride, an anhydro-derivative, $C_{11}H_{11}N_3O$, is formed; this crystallises in vitreous, lustrous needles melting at $88-89^\circ$, has well marked basic properties, readily dissolves in acids, and is reprecipitated by alkalis; attempts to regenerate the preceding yellow compound were unsuccessful.

Four different substances are formed by the interaction of phenylhydrazine and formazyl methyl ketone.

On allowing the substances to react at low temperatures in glacial acetic acid solution, *formazyl methyl ketone phenylhydrazone*,



is obtained, and crystallises in black, lustrous needles, with a dark steel blue reflex; it melts at 165° , and is soluble in chloroform, with a red colour.

Phenylazomethylsotriazone, $NPh < \begin{smallmatrix} N:CMe \\ N:C \end{smallmatrix} \cdot N \cdot NPh$, is formed by boiling formazyl methyl ketone with phenylhydrazine in acetic acid solution, or by heating the preceding compound for a short time at $170-180^\circ$; it crystallises in long, slender, golden-yellow, lustrous needles, melts at 122° , and is readily soluble in light petroleum or alcohol; the substance is a feeble base, and dissolves in concentrated sulphuric acid with a dark, orange-red colour.

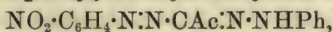
On heating formazyl methyl ketone with phenylhydrazine alone, nitrogen is evolved, and two compounds are formed; the one (m. p. 183°) is identical with the reduction product obtained by the action of ammonium sulphide (see above); the second is colourless and crystalline, and will be further investigated.

The purification of formazyl methyl ketone has hitherto been a matter of difficulty owing to the simultaneous formation of phenyl-azoformazyl; this can be avoided by the use of sodium carbonate solution instead of soda; the best method of preparation consists in treating pyruvic aldehyde hydrazone with concentrated aqueous diazobenzene at 0° ; the mixture is then gradually added to a well cooled solution of sodium carbonate.

Sodioformazyl methyl ketone, $\text{NPh}\cdot\text{N}\cdot\text{CAc}\cdot\text{N}\cdot\text{N}\cdot\text{NaPh}$, crystallises with 1 mol. of alcohol in red prisms, and is decomposed by water. The *potassium* derivative resembles the sodium salt. The *silver* and *copper* derivatives form dark-coloured powders.

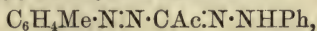
Diparatolyl formazyl methyl ketone, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{N}\cdot\text{CAc}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, is prepared from potassium acetoacetate, paradiazotoluene, and sodium acetate; it crystallises in slender, lustrous, brick-red needles melting at $153\text{--}154^{\circ}$; it is readily soluble in benzene, ether, and chloroform, and gives a blue coloration with concentrated sulphuric acid.

a-Paranitrophenyl-h-phenylformazyl methyl ketone,



is obtained from paranitrodiazotoluene and pyruvic aldehyde hydrazone, and crystallises in lustrous, dark, ruby-red needles which exhibit a steel-blue, metallic reflex; it melts at 180° , and is sparingly soluble in alcohol or ether. With concentrated sulphuric acid, a violet-red colour is formed.

a-Paratolyl-h-phenylformazyl methyl ketone,



is prepared from paradiazotoluene in a similar manner to the preceding compound; it crystallises in lustrous, dark garnet-red plates and melts at 126° . A reddish-violet coloration is produced with concentrated sulphuric acid.

Di- α -naphthylformazyl methyl ketone, $\text{C}_{10}\text{H}_7\text{N}\cdot\text{N}\cdot\text{CAc}\cdot\text{N}\cdot\text{NHC}_{10}\text{H}_7$, is formed by the action between potassium acetoacetate, α -diazonaphthalene, and sodium acetate; it is very sparingly soluble, is deposited in slender, dark green, lustrous needles, melts at $174\cdot5\text{--}175^{\circ}$, and gives a bluish-green colour with concentrated sulphuric acid.

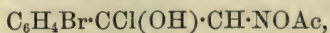
J. B. T.

Behaviour of certain Aromatic Isonitrosoketones towards Acetic Anhydride and Acetic Chloride. By H. G. SÖDERBAUM (*Ber.*, 25, 3459—3467; compare *Abstr.*, 1891, 1043).—The *acetyl* derivative of paratolulylformoxime (nitrosomethylparatolyl ketone, see Müller and v. Pechmann, *Abstr.*, 1890, 52), prepared by the action of acetic anhydride at the ordinary temperature, crystallises in large, rectangular tables, melts at $67\text{--}68^{\circ}$, and is converted into paratoluic acid and hydrogen cyanide by cold aqueous alkali hydroxides, alkali carbonates, or concentrated sulphuric acid. When heated on the water-bath for 2—3 hours with an excess of acetic anhydride, *paratolulyl cyanide*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CN}$, is formed; this crystallises in long, colourless prisms, melts at 52° , and is soluble in the ordinary solvents, water being an exception. It gives paratoluic acid on boiling with alkali, and its vapour has a pleasant odour. Paratolulylformoxime is readily soluble in acetic chloride, and, on cooling to 0° , an unstable chloride

separates which decomposes, when treated with water, into the *acetyl* derivative, $C_6H_4Me \cdot C(OH)_2 \cdot CH \cdot NOAc$; the latter melts at 148° , is readily soluble in alcohol, sparingly so in ether and benzene, and yields Claus and Kroseberg's paratolylhydroxyacetic acid (Abstr., 1887, 949) on treatment with cold sodium hydroxide, cold concentrated sulphuric acid, or boiling dilute hydrochloric acid.

Xyloylformoxime, $C_6H_3Me_2 \cdot CO \cdot CH \cdot NOH$ [$Me_2 : CO = 1 : 3 : 4$], prepared by Claisen's method from the corresponding xylyl methyl ketone, sodium ethoxide, and amyl nitrite, crystallises in long, delicate, white needles, and melts at $94-95^\circ$. Its *acetyl* derivative, $C_6H_3Me_2 \cdot CO \cdot CH \cdot NOAc$, obtained by the action of acetic anhydride in the cold, crystallises in white needles, melts at $53-54^\circ$, and, on hydrolysis with alkali, yields the acid $C_6H_3Me_2 \cdot COOH$, melting at 126° . The *cyanide*, $C_6H_3Me_2 \cdot CO \cdot CN$, is formed when the *acetyl* derivative is digested for 2—3 hours on the water-bath with acetic anhydride; it crystallises from light petroleum in long, white needles, melts at 47° , and is soluble in most organic solvents. The *acetyl* derivative, $C_6H_3Me_2 \cdot C(OH)_2 \cdot CH \cdot NOAc$, obtained from xyloylformoxime and acetic chloride, crystallises from chloroform in small, white needles, melts at 142° , and yields *dimethylmandelic* acid together with xylylformoin (see this vol., i, 169) on treatment with cold alkali. The dimethylmandelic acid crystallises in thin, six-sided, colourless leaflets, and melts at 103° .

Parabromobenzoylformoxime, $C_6H_4Br \cdot CO \cdot CH \cdot NOH$, obtained from acetyl bromobenzene (Schweitzer, Abstr., 1891, 684), sodium ethoxide, and amyl nitrite, crystallises in flat, lustrous, yellowish needles, and melts at 164° . The *acetyl* derivative, $C_6H_4Br \cdot CO \cdot CH \cdot NOAc$, crystallises from methyl alcohol in stout, four-sided tables, melts at 89° , and yields parabromobenzoic acid (m. p. $251-252^\circ$) on hydrolysis with alkali. Parabromobenzoic acid is also the chief product when the oxime is boiled with acetic anhydride. A *chloride*,



is formed when finely powdered parabromobenzoylformoxime is mixed with acetic chloride, and allowed to remain therewith; it commences to sinter at 120° , but only fuses completely at 150° . On treatment with water, it yields the *acetyl* derivative, $C_6H_4Br \cdot C(OH)_2 \cdot CH \cdot NOAc$, which crystallises in small, white needles, melts at about 153° , and is converted into *parabromomandelic* acid on hydrolysis with alkali. The latter crystallises in delicate, white needles, and melts at $117-118^\circ$.

A. R. L.

Preparation and Nitration of Orthochlorobenzaldehyde. By H. ERDMANN (*Annalen*, 272, 148—156).—In chlorinating the chlorotoluenes at a high temperature, the substitution of the hydrogen atoms of the side chain takes place three or four times more quickly when 2 to 3 per cent. of phosphorus pentachloride is added as a chlorine carrier; the reaction must also be carried out in bright daylight, and the gas employed be quite dry and in a fine stream, otherwise most of the chlorine passes through the liquid without being absorbed.

For the preparation of orthochlorobenzaldehyde, dry orthochlorotoluene (750 grams) is chlorinated at $150-180^\circ$ under the conditions

just mentioned, the process being interrupted as soon as a gain in weight of 380—400 grams has taken place. The crude orthochlorobenzalchloride (1100 grams) is then stirred with a cold mixture of concentrated sulphuric acid (2200 grams) and 10 per cent. anhydrosulphuric acid (2200 grams) in a vessel surrounded by water; after a few minutes, evolution of hydrogen chloride sets in and the temperature of the mixture gradually falls from about 21° to 11.5° in the course of an hour. After stirring for about six hours, the mixture is placed in a separating funnel and kept over night; the acid solution of the chlorobenzaldehyde is then run on to ice, the aldehyde separated, washed, dried, and repeatedly fractionated. The yield of chlorobenzaldehyde, collected within a range of $2\frac{1}{2}^{\circ}$, is about 170 grams, and further quantities can be obtained from the other fractions.

Nitrochlorobenzaldehyde [$\text{Cl} : \text{CHO} : \text{NO}_2 = 1 : 2 : 4$], prepared from chlorobenzaldehyde, crystallises in stellar groups of needles or in plates, melts at 80° , and forms an *oxime* melting at 147 — 148° . On oxidation with potassium permanganate, it is converted into the corresponding chloronitrobenzoic acid, and when its diazo-derivative is decomposed with cuprous chloride, paradichlorobenzaldehyde is formed.

F. S. K.

Aluminium Chloride and Nitro-compounds. By F. STOCKHAUSEN and L. GATTERMANN (*Ber.*, 25, 3521—3525).—The aluminium chloride employed in these experiments was specially prepared by passing hydrogen chloride over aluminium turnings heated in a wide combustion tube, by which means it can readily be obtained quite pure in fairly large quantities. The pure compound is much more active than the commercial article, the reactions proceeding more quickly and giving better yields, whilst some reactions which do not take place when the crude compound is employed can be readily carried out with the pure substance.

Aluminium chloride reacts very violently when mixed with nitrobenzene, carbonisation taking place to a large extent; if, however, the nitrobenzene is diluted with light petroleum, the two compounds unite in molecular proportion, forming a crystalline substance; other nitro-derivatives behave in a similar manner.

All attempts to carry out the Friedel-Crafts ketone synthesis by the action of aluminium chloride on a mixture of a nitro-compound and acetic chloride were without success. On the other hand, the reaction may be carried out if the nitro-derivatives of the phenol ethers be substituted for those of the hydrocarbons. Thus nitranisöl and acetic chloride when treated with aluminium chloride in carbon bisulphide solution yield *acetonitranisöl*, $\text{MeO} \cdot \text{C}_6\text{H}_3\text{Ac} \cdot \text{NO}_2$, which crystallises from alcohol in long, colourless needles melting at 99.5° . The yield is, however, small, as the nitranisöl is itself hydrolysed by the action of the aluminium chloride, the liquid containing, in addition to the above compound, orthonitrophenol and nitrohydroxyacetophenone. The acetyl group in these compounds probably occupies the para-position relatively to the methoxyl group. Orthonitrophenetoil yields a similar ketone, $\text{EtO} \cdot \text{C}_6\text{H}_3\text{Ac} \cdot \text{NO}_2$, which crystallises in colourless needles and melts at 66 — 67° .

H. G. C.

Aromatic Alkyl Ketones. By A. CLAUS (*J. pr. Chem.* [2], **46**, 474—496; compare Abstr., 1891, 1222; 1892, 985).—*Metaxylyl propyl ketone* [$\text{Me}_2 : \text{COPr}^a = 1 : 3 : 6$] is a colourless, refractive, aromatic, oily liquid; it boils at 251° (uncorr.), and dissolves in the usual solvents except water. By oxidation with potassium permanganate it yields orthoparadimethylbenzoylformic acid (metaxylyl glyoxylic acid, Abstr., 1891, 564). By reduction in alkaline solution it yields *metaxylylpropylcarbinol* [$\text{Me}_2 : \text{CHPr}^a\text{OH} = 1 : 3 : 6$], which is a yellow oil, and boils above 270° . The *oxime* was also prepared. *Metaxylylbutyramide*, $\text{C}_6\text{H}_3\text{Me}_2[\text{CH}_2]_3\text{CONH}_2$ [$= 1 : 3 : 6$], was prepared from the ketone by Willgerodt's reaction (heating with yellow ammonium sulphide containing sulphur); it crystallises in colourless, flat needles, melts at $123\text{--}124^\circ$, and dissolves in most solvents. *Metaxylylbutyric acid* crystallises in colourless needles, and melts at 70° ; its *potassium*, *sodium*, *barium* (with $4\text{H}_2\text{O}$), *calcium* (with $4\text{H}_2\text{O}$), *copper*, *lead*, and *silver* salts were prepared.

Paraxylyl propyl ketone [$\text{Me}_2 : \text{COPr}^a = 1 : 4 : 2$] is a colourless, oily liquid, of characteristic odour and lower sp. gr. than water; it boils at 249° . The *oxime* forms thick, colourless needles, and melts at 47° . *Paraxylylbutyramide* (m. p. 125°) and *paraxylylbutyric acid* (m. p. 70°) are similar in all respects to the metaxylyl derivatives (see above); the same salts were prepared and found to contain the same water of crystallisation.

Tolyl isopropyl ketone [$\text{Me} : \text{COPr}^b = 1 : 4$] is a colourless, refractive liquid, of aromatic odour and bitter taste; it boils at $235\text{--}236^\circ$. The *oxime* crystallises in colourless, hexagonal tables and in flat needles, and melts at 92° . By reduction with sodium amalgam, the ketone yields an oil which crystallises and then melts at 199° ; when zinc and alcoholic potassium hydroxide are used, *tolylisopropylcarbinol* is obtained; this is a thick, yellowish-brown oil, which boils above 300° . By oxidation with alkaline potassium permanganate, the ketone yields only paratoluic and terephthalic acids.

Metaxylyl isopropyl ketone [$\text{Me}_2 : \text{COPr}^b = 1 : 3 : 6$] is a colourless oil which boils at $244\text{--}245^\circ$. The *phenylhydrazide* melts at $128\text{--}129^\circ$, and the *oxime* at 97° . The reduction products (compare above) melt at 110° and boil about 300° respectively, but are not yet identified. Oxidation of the ketone by dilute aqueous potassium permanganate yields metaxylyl glyoxylic acid; this is the first isopropyl ketone in which the authors have observed an oxidation of the secondary alkyl group to carboxyl with formation of the corresponding α -ketonic acid. The ketone can, with difficulty, be converted into *metaxylyl isobutyramide* [$\text{Me}_2 : \text{CH}_2\cdot\text{CHMe}\cdot\text{CONH}_2 = 1 : 3 : 6$], and the yield is small; this compound crystallises in needles and melts at 120° ; the corresponding *acid* forms colourless, nacreous crystals, and melts at 70° .

Paraxylyl isopropyl ketone [$\text{Me}_2 : \text{COPr}^b = 1 : 4 : 2$] is a colourless oil having a mushroom-like odour and bitter taste; it boils at $239\text{--}240^\circ$. The *oxime* crystallises in small tables and prisms, and melts at 76° .

Orthoxylyl isopropyl ketone [$\text{Me}_2 : \text{COPr}^b = 1 : 2 : 4$], is a colourless oil of faint turpentine-like odour, and boils at $255\text{--}258^\circ$. The *oxime* forms large, vitreous prisms, and melts at 68° . Oxidation of the

ketone with aqueous potassium permanganate yields no ketonic acid but plenty of metaparadimethylbenzoic acid (m. p. 163°).

Paraisocymyl isopropyl ketone [$\text{Me} : \text{Pr}^\beta : \text{COPr}^\beta = 1 : 4 : 2$] is a pale yellow, oily liquid of sp. gr. 0.957 at 19°, and boils at 259°. The *phenylhydrazide* is a yellow oil which cannot be crystallised. The *oxime* is a pale yellow oil which, like the oximes of other ketones containing isocymyl, cannot be crystallised. When the ketone is reduced with iodine and phosphorus (compare Abstr., 1892, 985), *orthoisobutylparaisopropyltoluene* [$\text{Me} : \text{Pr}^\beta : \text{CH}_2\text{Pr}^\beta = 1 : 4 : 2$] is obtained; it is a colourless liquid of sp. gr. 0.916 at 17°, and boils at 230°.

Paraisocymyl ethyl ketoxime is a yellow, uncrystallisable oil.

Orthopropylparaisopropyltoluene [$\text{Me} : \text{Pr}^\alpha : \text{Pr}^\beta = 1 : 2 : 4$] is a colourless, refractive liquid of sp. gr. 0.902 at 17°, and boils at 225°.

Isocymyl propyl ketoxime is a viscid oil.

Orthobutylparaisopropyltoluene [$\text{Me} : \text{Pr}^\beta : \text{C}_4\text{H}_9 = 1 : 4 : 2$] is a colourless, refractive liquid, of sp. gr. 0.892 at 17°, and boils at 235°.

Paraisocymyl isobutyl ketone [$\text{Me} : \text{Pr}^\beta : \text{CO}\cdot\text{C}_4\text{H}_9 = 1 : 4 : 2$] is a nearly colourless, refractive oil of sp. gr. 0.944 at 19°, and boils at 270—272°. The *phenylhydrazide* is a dark red oil; the *oxime* is a pale yellow, viscid oil. By reduction with phosphorus and iodine, the ketone yields *orthoisoamylparaisopropyltoluene* [$\text{Me} : \text{Pr}^\beta : \text{C}_5\text{H}_{11} = 1 : 4 : 2$], a colourless, mobile oil, which boils at 245°, and has sp. gr. 0.89 at 17°.

Phenyl isobutyl ketone has been described before (*Beilstein* [2], 3, 84); its *oxime* melts at 74°. Isoamylbenzene is also known (*loc. cit.*, p. 26).

Metacymyl methyl ketone [$\text{Me} : \text{Pr}^\alpha : \text{COMe} = 1 : 3 : 4$] is a colourless liquid, specifically lighter than water; it boils at 248—252°. The *oxime* is a yellow, viscid oil. *Metacymylglyoxylic acid* [$\text{Me} : \text{Pr}^\alpha : \text{CO}\cdot\text{COOH} = 1 : 3 : 4$] is described, together with its *barium* (with H_2O), *calcium* (with $2\text{H}_2\text{O}$), and *copper* salts. *Metacymylcarboxylic acid* [$\text{Me} : \text{Pr}^\alpha : \text{COOH} = 1 : 3 : 4$] melts at 75—76°; its *barium* (with $1\frac{1}{2}\text{H}_2\text{O}$) and *calcium* (with $2\text{H}_2\text{O}$) salts were prepared. These two acids are the products of the partial oxidation of the ketone with potassium permanganate; ultimately trimellitic acid is produced.

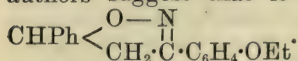
A. G. B.

Aromatic Ketones. By F. STOCKHAUSEN and L. GATTERMANN (*Ber.*, 25, 3535—3538).—No ketones have hitherto been prepared from unsaturated acids by Friedel and Craft's method; the authors find, however, that the synthesis can be accomplished without difficulty.

By the action of cinnamic chloride and ethoxybenzene dissolved in carbon bisulphide on aluminium chloride at ordinary temperatures, a ketone is obtained which has the formula $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$; it forms colourless crystals, and melts at 74—75°. On treatment with bromine at the ordinary temperature, an additive compound, $\text{C}_{17}\text{H}_{16}\text{Br}_2\text{O}_2$, is obtained which forms colourless crystals, and melts at 150°.

By the action of hydroxylamine on the ketone in alkaline solution,

a compound is obtained which crystallises in small plates melting at 107—108°; it does not appear to be an oxime, since it is not hydrolysed by heating with hydrochloric acid in a sealed tube; it is insoluble in alkali, and yields no acetate on treatment with acetic anhydride, the authors suggest that it is probably represented by the formula



A corresponding *methoxy-derivative*, $\text{CHPh} \cdot \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, is prepared from cinnamic chloride and methoxybenzene; it crystallises in colourless needles melting at 106—107°. The *dibromo-compound*, $\text{C}_{16}\text{H}_{14}\text{O}_2\text{Br}_2$, forms needles which melt at 158—159°. With hydroxylamine, a substance is obtained which is analogous to the ethoxy-derivative, and crystallises in pearly, lustrous plates melting at 122—123°.

Cinnamic chloride and α -ethoxynaphthalene also yield a ketone which crystallises from alcohol in needles melting at 85—86°.

Phenylpropionic chloride, $\text{CPh} \cdot \text{C} \cdot \text{COCl}$, is prepared from phenylpropionic acid and phosphoric chloride; it is a colourless liquid which boils at 130—133° under a pressure of 25—30 mm., and solidifies on cooling. The *amide*, $\text{CPh} \cdot \text{C} \cdot \text{CO} \cdot \text{NH}_2$, crystallises from water in colourless needles melting at 99—100°. The *anilide* is deposited in needles which melt at 125—126°. On treating phenylpropionic chloride with methoxybenzene and aluminium chloride, a ketone, $\text{CPh} \cdot \text{C} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, is obtained which crystallises in colourless needles melting at 100°. By the action of bromine at the ordinary temperature, a dibromo-additive compound, $\text{C}_{16}\text{H}_{12}\text{O}_2\text{Br}_2$, is formed; it forms colourless crystals, and melts at 138—140°.

The authors failed to obtain ketones by the action of aromatic hydrocarbons on cinnamic chloride in presence of aluminium chloride.

J. B. T.

Azoxybenzoic acids. By N. N. USPENSKY (*J. Russ. Chem. Soc.*, 23, 89—92).—10 grams of orthonitrobenzoic acid, 10 grams of potash in small pieces, and 10 grams of alcohol were heated together, and the alcohol distilled off after the completion of the reaction. The residue was dissolved in water, and precipitated with hydrochloric acid. The impure orthazoxybenzoic acid thus obtained was purified by conversion into the soluble barium salt, from solutions of which the acid may be precipitated in the crystalline form.

The pure acid, $\text{ON}_2(\text{C}_6\text{H}_4 \cdot \text{COOH})_2$, forms large, prismatic, transparent, brownish-yellow crystals belonging to the triclinic system. It is very soluble in boiling alcohol, but only slightly soluble in ether or in boiling water. At 200°, it begins to decompose, and at 237°, melts with formation of a black mass. The methyl salt, prepared by passing hydrogen chloride into a solution of the acid in methyl alcohol, is a solid which crystallises from alcohol in long, golden-yellow prisms, and melts at 115.5°.

40 grams of metanitrobenzoic acid, 40 grams of potash, and 300 grams of alcohol were heated for 12 hours, using a reflux condenser. The crude metazoxybenzoic acid obtained after distilling off the alcohol and precipitating with hydrochloric acid, was purified by dissolving

it in ammonia, and precipitating the acid impurities by means of calcium chloride. The filtrate, on treatment with hydrochloric acid, gave about half the theoretical quantity of metazoxybenzoic acid in the form of a slightly yellow, amorphous mass, insoluble in water, alcohol, and ether. From boiling acetic acid, it separates in the form of yellow, microscopic prisms. Large crystals may be obtained by dissolving the acid in acetic acid at 200° in a sealed tube, and allowing it to cool very slowly. It melts at 320° with decomposition, the upper part of the tube becoming covered with a white deposit.

By employing sodium methoxide and methyl alcohol instead of potash and ethyl alcohol in the preparation of the azoxybenzoic acids, a better yield of pure substance is obtained. Thus 40 grams of meta-nitrobenzoic acid, boiled for 20 hours in a solution of 30 grams of sodium in 250 grams of methyl alcohol, gave 25 grams of almost colourless metazoxybenzoic acid. 10 grams of the orthonitro-acid, similarly treated, gave 8 grams of the pure azoxy-acid. Paranitrobenzoic acid, under the same circumstances, gave no azoxy-acid, but a good yield of pure parazobenzoic acid. J. W.

Action of Phosphorus Pentachloride on Azo- and Azoxybenzoic acids. By N. N. USPENSKY (*J. Russ. Chem. Soc.*, 23, 92—94).—Parazobenzoic acid was heated in a flask with twice its weight of phosphorus pentachloride until the whole fused to a homogeneous, coloured liquid, which solidified to a crystalline mass on cooling; this was washed with ether in order to remove phosphorus oxychloride, and recrystallised from benzene or light petroleum. The red needles thus obtained were crystals of the acid chloride, $N_2(C_6H_4COCl)_2$, easily soluble in benzene and light petroleum, soluble with difficulty in ether, and melting at 144.5 — 145° . With ethyl alcohol, the acid chloride at once gives the corresponding ethyl salt, which melts at 114.5° .

Metazobenzoic acid, when treated in like manner, gives an acid chloride melting at 97° .

Metazoxybenzoic acid gives an acid chloride which crystallises in almost colourless needles, easily soluble in benzene, and melting at 120 — 121.5° . The ethyl salt obtained from the acid chloride melts at 76 — 78° .

Orthazoxybenzoic acid reacts violently in the cold with phosphorus pentachloride, with formation of a tarry mass. When the action takes place in presence of a large quantity of benzene, a crystalline mass of yellow needles is obtained. These needles melt at 210° , but only contain 13.10 per cent. of chlorine instead of the 21.98 per cent. demanded by the formula $N_2O(C_6H_4COCl)_2$. The author considers them to be the half acid chloride $COCl \cdot C_6H_4 \cdot N_2O \cdot C_6H_4 \cdot COOH$.

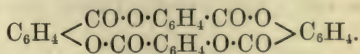
Orthazobenzoic acid yields no crystalline substance with phosphorus pentachloride, either by itself or in presence of benzene. J. W.

Salicylide. By R. ANSCHÜTZ (*Ber.*, 25, 3506—3512).—Up to the present, only one member of the lactide group has been definitely prepared, namely, lactide itself; glycolide, from its physical properties, must have a higher molecular weight than is indicated by the

formula $\text{CH}_2\langle\begin{smallmatrix}\text{CO}\cdot\text{O} \\ \text{O}\cdot\text{CO}\end{smallmatrix}\rangle\text{CH}_2$. In the aromatic group, the only known substance which might belong to this group is the so-called salicylide obtained by the action of phosphorus oxychloride on salicylic acid; this substance, however, as hitherto prepared, is not a homogeneous compound. The author has now succeeded in obtaining it in a pure condition, by dissolving salicylic acid in toluene or xylene, and gradually adding an equal weight of phosphorus oxychloride to the warmed solution. When crystallised from chloroform, it forms transparent, tetragonal crystals ($a : c = 1 : 1.4530$), which contain chloroform and have the formula $\text{C}_{28}\text{H}_{16}\text{O}_8, 2\text{CHCl}_3$. On heating, chloroform is evolved and salicylide remains as a white substance, which melts at $261\text{--}262^\circ$, is very slightly soluble in the usual solvents, and is gradually converted by boiling soda into salicylic acid. The residue left after extraction with chloroform is scarcely soluble in the ordinary solvents, but separates from phenol and nitrobenzene in microscopic needles which melt at $322\text{--}325^\circ$ without evolution of gas. It has the same composition as salicylide, and, like the latter, is converted into salicylic acid by long continued boiling with alkalis; it may, therefore, be termed *polysalicylide*, $(\text{C}_7\text{H}_4\text{O}_2)_n$.

Orthohomosalicylic acid, when treated with phosphorus oxychloride, also yields a similar *orthohomosalicylide*, $\text{C}_{28}\text{H}_{12}\text{Me}_4\text{O}_8$, which separates from chloroform in tetragonal crystals, likewise containing chloroform, which is evolved at 100° ; the residual orthohomosalicylide is even less soluble than salicylide, and melts at $293\text{--}295^\circ$. Metahomosalicylic acid only yields a compound corresponding with polysalicylide, $(\text{C}_7\text{H}_3\text{MeO}_2)_n$, which is insoluble in chloroform, and after crystallisation from phenol melts at $292\text{--}294^\circ$. *Parahomosalicylide*, obtained from parahomosalicylic acid, melts at $295\text{--}297^\circ$, and although soluble in boiling chloroform, does not yield crystals containing that substance.

The determination of the molecular weight of salicylide and its homologues in phenol solution leads to the supposition that they contain the group $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CO} \\ \text{O}\end{smallmatrix}\rangle$ four times; the constitution of salicylide is possibly represented by the formula

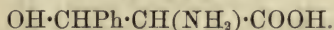


The molecular weight of the poly-derivatives could not be ascertained, but lactide gave numbers in phenol solution corresponding with the formula $\text{C}_6\text{H}_8\text{O}_4$, whilst glycolide appears to be $(\text{C}_2\text{H}_2\text{O}_2)_6$. The author proposes, therefore, that lactide should be termed *dilactide*, salicylide *tetrasalicylide*, and so on.

H. G. C.

New Phenylamidolactic acid from Glycocine and Benzaldehyde. By E. ERLÉNMEYER, Jun. (*Ber.*, 25, 3445—3447).—Benzaldehyde and glycocine, in dilute alcoholic solution, and in presence of sodium hydroxide, form condensation products; from these, boiling alcohol extracts a compound which is under investigation, whilst the residue consists of a sodium salt sparingly soluble in water. On treatment with acetic acid, the latter decomposes, yielding benz-

aldehyde, and if the product is passed through a wet filter, the last-named compound is retained by it; the filtrate, when concentrated, yields phenylamidolactic acid (phenylserine),



It crystallises in lustrous leaflets with 1 mol. H_2O , melts with decomposition at $192\text{--}193^\circ$, or after drying at 100° at $195\text{--}196^\circ$; it is sparingly soluble in water, and almost insoluble in alcohol. When the acid is treated with potassium nitrite and hydrochloric acid, ether extracts phenylglyceric acid, and on warming the latter with concentrated sulphuric acid, it is converted into a compound giving, with ferric chloride, the green colour reaction characteristic of phenylpyruvic acid.

By condensing benzaldehyde with hippuric acid, a *lactimide*, probably $\text{CPhO} \cdot \text{N} < \begin{smallmatrix} \text{C}(\text{CHPh}) \cdot \text{CO} \\ \text{CO} \cdot \text{C}(\text{CHPh}) \end{smallmatrix} > \text{N} \cdot \text{CPhO}$, is obtained, and an acetylbenzoyl derivative of the above described phenylamidolactic acid is perhaps an intermediate product of the reaction. In support of this view, it is found that this phenylamidolactic acid, when heated with acetic anhydride and sodium acetate, yields a lactimide closely resembling that mentioned above. The author hopes to be able to synthesise serine from formaldehyde and glycocine.

A. R. L.

Methylation of Opianic acid. By R. WEGSCHEIDER (*Monatsh.*, **13**, 702—715; compare Abstr., 1892, 1208).—The author has investigated the action of methyl iodide on lead opianate; of methyl alcohol on opianic chloride; and, lastly, of methyl alcohol on (1) opianic acid and (2) its methyl salt, in presence of hydrochloric acid. The results obtained show that in every case the formation of the pseudomethyl salt, $\text{C}_6\text{H}_2(\text{OMe})_2 < \begin{smallmatrix} \text{CH}(\text{OMe}) \\ \text{CO} \end{smallmatrix} > \text{O}$, which melts at 103° , depends on the attachment of the methyl alcohol to the COH group. When this reaction is prevented, the formation of the true methyl salt, $\text{CHO} \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{COOH}$, invariably follows.

G. T. M.

Anilide of Gallic acid. By H. SCHIFF (*Annalen*, **272**, 234—238).—*Gallanilide*, $\text{C}_6\text{H}_2(\text{OH})_3 \cdot \text{CO} \cdot \text{NHPh} + \text{H}_2\text{O}$, can be obtained by heating tannin with anhydrous aniline sulphite (compare *Annalen*, **140**, 126) at $90\text{--}120^\circ$, and crystallising the solid product from dilute sulphurous acid; it is then treated with dilute ammonium carbonate to free it from gallic acid. It forms large, lustrous, colourless plates, melts at 207° , loses its water at 100° , and gives a red coloration with alkalis; in very dilute solutions, ferric chloride produces a violet, in more concentrated solutions a bluish-green coloration. The *triacetyl* derivative, $\text{C}_6\text{H}_2(\text{OAc})_3 \cdot \text{CO} \cdot \text{NHPh}$, crystallises from dilute alcohol in colourless, concentrically-grouped needles, and melts at $101\text{--}102^\circ$.

Aniline gallate, $\text{NH}_2\text{Ph} \cdot \text{C}_7\text{H}_6\text{O}_5$, is formed when gallic acid is heated with aniline at 100° ; it crystallises from water and from alcohol, melts at 168° with decomposition into its components, and is slowly decomposed by boiling water.

F. S. K.

Synthesis of Symmetrical Diphenylsulphoneacetone by means of Symmetrical Dichloroacetone. By R. OTTO and J.

TRÖGER (*Ber.*, **25**, 3422—3425; compare *Abstr.*, 1889, 1186).—Symmetrical diphenylsulphoneacetone is obtained by boiling dichloroacetone dissolved in benzene for several days in a reflux apparatus with anhydrous sodium benzenesulphinate; the intermediate compound, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{CH}_2\text{SO}_2\text{Ph}$, is also formed; it gives methylphenylsulphone (m. p. 88—89°) on treatment with alkali. Diphenylsulphoneacetone is also produced, together with other compounds, by oxidising dithiophenylacetone dissolved in benzene with potassium permanganate and sulphuric acid. The dithiophenylacetone is obtained by the action of the sodium derivative of thiophenol on dichloroacetone in alcoholic solution. A. R. L.

Nitrosulphonic acids. By H. LIMPRICHT (*Ber.*, **25**, 3477).—The author finds that the compound described by him as nitrosobenzene-sulphonic acid (*Abstr.*, 1892, 475) is a nitrobenzenesulphinic acid. The nitrosulphonic acids which have been examined, namely, metanitrosulphinic, ortho- and para-nitrotoluenesulphinic, and nitronaphthalenesulphinic acids, all give a blue colour with phenol and sulphuric acid, similar to that obtained with nitroso-compounds. Metanitrobenzene sulphobromide also gives a blue coloration with phenol and sulphuric acid, but the sulphochloride does not. E. C. R.

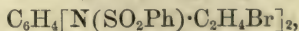
Benzenesulphonamides. By O. HINSBERG (*Annalen*, **272**, 229—233; compare *Abstr.*, 1892, 64).—*Benzenesulphoneamidoazobenzene*, $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$, prepared by warming benzenesulphonic chloride with amidoazobenzene in benzene solution, crystallises from dilute alcohol in yellowish needles, and melts at 133°; it forms a yellow, sparingly soluble sodium derivative.

Dibenzenesulphonebenzidine, $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{C}_{12}\text{H}_8\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$, is formed when finely-divided benzidine is shaken with soda and benzenesulphonic chloride; it is a colourless, crystalline substance, melts at 232°, and is only sparingly soluble in all ordinary solvents.

Benzenesulphonebenzidine, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$, is also produced under the conditions first mentioned, and can be separated from the preceding compound by solution in hydrochloric acid; it crystallises from dilute alcohol in colourless needles melting at 160—161°.

Dibenzenesulphonedimethylbenzidine, $\text{C}_{26}\text{H}_{24}\text{N}_2\text{S}_2\text{O}_4$, is obtained when dibenzenesulphonebenzidine is treated with methyl iodide and soda in alcoholic solution; it crystallises in small, colourless needles, and melts at 179—180°.

Dibromodiethyldibenzenesulphoneparaphenylenediamine,



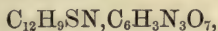
is formed when dibenzenesulphoneparaphenylenediamine is treated with ethylene bromide and alcoholic potash; it crystallises from hot ethylene bromide in colourless prisms, and melts at 192°.

F. S. K.

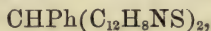
Thienylindole, α -Naphthylindole, and some Bromo-derivatives of Indoles. By K. BRUNCK (*Annalen*, **272**, 201—208).—

Thienylindole, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH} \\ \text{NH} \end{smallmatrix}\rangle\cdot\text{C}_4\text{SH}_3$, is formed when acetothienone-

hydrazone is heated with anhydrous zinc chloride, it crystallises from alcohol in yellow needles, melts at 162° , sublimes readily, and gives a bluish-violet pine-chip reaction. The *picrate*,



crystallises in dark red plates melting at 137° . The *nitroso*-derivative, $\text{C}_{12}\text{H}_8\text{N}_2\text{SO}$, separates from boiling glacial acetic acid in microscopic, orange-red plates, darkens at 230° , and melts at 240 – 241° when quickly heated; it is moderately easily soluble in alkalis, and does not give Liebermann's reaction. The *benzal* derivative,



crystallises from a mixture of alcohol and acetone in yellow plates, melts at 245° with decomposition, and is decomposed by hot concentrated hydrochloric acid.

α -Naphthylindole, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH} \\ \text{NH}\end{smallmatrix}\rangle\text{C}\cdot\text{C}_{10}\text{H}_7$, prepared by heating the hydrazone of methyl naphthyl ketone with zinc chloride, crystallises from alcohol in pale yellow, concentrically grouped needles, and melts at 196° . The *picrate*, $\text{C}_{24}\text{H}_{16}\text{N}_4\text{O}_7$, forms purple-red scales, and melts at 179° . The *nitroso*-derivative, $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}$, crystallises from glacial acetic acid in yellowish-red plates, and melts at 248° with decomposition. The *benzal* derivative, $\text{CHPh}(\text{C}_{18}\text{H}_{12}\text{N})_2$, separates from acetone in reddish plates melting at 246° .

A *bromo*-derivative, which is probably a tetrabromophenylindole dibromide, $\text{C}_{14}\text{H}_7\text{NBr}_6$, is formed when a chloroform solution of phenylindole is gradually added to a large excess of bromine and the mixture then carefully warmed; it crystallises from hot benzene in colourless, well-defined plates melting at 259 – 260° . It does not form a compound with picric acid, does not show the pine-chip reaction, and is not acted on by boiling hydrochloric acid or boiling nitric acid.

The *bromo*-derivative of the composition $\text{C}_{12}\text{H}_5\text{NSBr}_6$, prepared from thienylindole in like manner, separates from benzene in plates, and melts at 278° ; the compound of the composition $\text{C}_{18}\text{H}_9\text{NBr}_6$, obtained from α -naphthylindole, crystallises in yellow plates melting above 300° .

When methylketole (methylindole) is treated with excess of bromine at the ordinary temperature, it yields two products, one of which crystallises from glacial acetic acid in yellowish needles, melts at 195° , and has the composition $\text{C}_9\text{H}_7\text{NBr}_4$; the other product is insoluble in glacial acetic acid, and melts above 300° . F. S. K.

Aromatic Tetraketones. By P. W. ABENIUS and H. G. SÖDERBAUM (*Ber.*, 25, 3468–3476).—The authors find that the reaction by which the hydrate of an acetylated aromatic isonitrosoketone when treated with sodium carbonate is converted into a hydroxytriketone is of general application.

Diphenylhydroxytriketone, when treated with hydroxylamine hydrochloride in alcoholic solution, yields the anhydrides of its mono- and di-oxime, a compound $\text{C}_{18}\text{H}_{16}\text{O}_4$, and also a small quantity of the dioxime of the tetraketone, which remains in the mother liquors.

The above three compounds are separated partly by fractional crystallisation from alcohol and partly by mechanical means.

The *anhydride of the monoxime*, $\text{CPh}\cdot\text{CO}\begin{smallmatrix} \text{||} \\ \text{N} \end{smallmatrix}\text{---O} > \text{CH}\cdot\text{CPhO}$, crystallises in beautiful, yellow, lustrous scales, melts at 175° , and darkens slightly on exposure to light.

The *anhydride of the dioxime*, $\text{CPh}\cdot\text{CO}\begin{smallmatrix} \text{||} \\ \text{N} \end{smallmatrix}\text{---O} > \text{CH}\cdot\text{CPh}\cdot\text{NOH}$, crystallises in thick, pale yellow rhombohedra, sinters at 185° , melts at 191° with decomposition, and turns brownish-yellow on exposure to light.

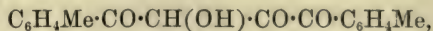
The compound $\text{C}_{18}\text{H}_{16}\text{O}_4$ crystallises in thick, yellow, rhombic prisms. It is also obtained by reducing diphenylhydroxytriketone with stannous chloride and hydrochloric acid. The *acetyl derivative*, $\text{C}_{20}\text{H}_{18}\text{O}_5$, crystallises in short, white aggregates of prisms, and melts at $121\text{--}122^\circ$.

Diphenyltetraketonedioxime, $\text{C}_2\text{O}_2(\text{CPh}\cdot\text{NOH})_2$, is easily obtained by warming the tetraketone (Abstr., 1892, 69) with hydroxylamine hydrochloride in alcoholic solution. It crystallises with 1 mol. of alcohol in colourless prisms, melts at 176° with evolution of gas, and when heated at 190° yields benzonitrile and oxalic acid, showing that the carbonyl groups which have reacted with hydroxylamine are those united to phenyl.

Benzoylformoxime, when treated with phenylhydrazine acetate in alcoholic solution, yields a brownish, resinous product, from which a small quantity of a crystalline substance melting at 262° can be isolated.

Diphenyltetraketone and phenylhydrazine acetate yield two crystalline compounds which may be separated by crystallisation from ether. The one, easily soluble in ether, crystallises in slender, lustrous needles, and melts at 167° ; the other, sparingly soluble in ether, crystallises in colourless needles, and melts at 184° .

Diparatoluylylhydroxytriketone,



forms yellow, microscopic crystals, turns red at 140° , and melts at 161° to a red liquid. It has feeble acid properties, and dissolves in alkalis with an intense, reddish-yellow coloration.

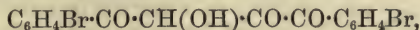
Diparatoluylyltetraketone hydrate, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{C}(\text{OH})_2\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$, crystallises in long, sulphur-yellow prisms, melts at 88° , and sometimes crystallises from carbon bisulphide in beautiful, thick prisms containing carbon bisulphide. The *dioxime*, $\text{C}_2\text{O}_2[\text{C}(\text{NOH})\cdot\text{C}_6\text{H}_4\text{Me}]_2$, crystallises in lustrous, colourless leaflets containing 1 mol. of alcohol, and melts at 181° with decomposition.

Diaryllylhydroxytriketone, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_3\text{Me}_2$, crystallises in slender needles, and melts at 155° .

Diaryllyltetraketone, $\text{C}_4\text{O}_4(\text{C}_6\text{H}_3\text{Me}_2)_2$, crystallises in lustrous, scarlet needles, melts at 180° , is indifferent to alkalis and acids, and is sparingly soluble in the ordinary solvents. The *dihydrate* is obtained by adding a large quantity of water to a solution of the tetraketone.

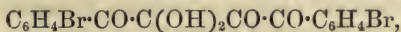
in acetic acid; it crystallises in short, four-sided, yellow prisms, and gradually loses water at 100°, being reconverted into the tetraketone.

Diparabromophenylhydroxytriketone,



crystallises in small prisms or rectangular tablets, reddens at 110°, and melts at 180°.

Diparabromophenyltetraketone hydrate,



crystallises in yellow needles, and, at 135°, melts to a yellow liquid with evolution of gas. E. C. R.

Acetyl Derivatives of 2:1-Amidonaphthol. By O. MICHEL and E. GRANDMOUGIN (*Ber.*, 25, 3429—3434).—When 2:1-amidonaphthol hydrochloride is dissolved in water with the addition of concentrated hydrochloric acid, and binormal nitrite solution added at 0°, β -naphthaquinone is the sole product as previously shown (*Abstr.*, 1892, 832). Meldola and Morgan (*Trans.*, 1889, 120) stated that they obtained nitroso- β -naphthol by the action of nitrous acid on 2:1-amidonaphthol (Meldola has since confirmed the authors' statement that the product is β -naphthaquinone, *Proc.*, 1892, 218).

When 2:1-amidonaphthol hydrochloride is warmed for about two minutes with acetic anhydride, the diacetyl derivative (Meldola and Mozgan, *loc. cit.*) is exclusively formed, whilst by continuing the heating for $3\frac{1}{2}$ —4 hours ethenylamidonaphthol (Böttcher, *Abstr.*, 1883, 1113) is also one of the products, and when the mixture is heated in a sealed tube at 130—140° for $1\frac{1}{2}$ hours, a certain quantity of acetamido- β -naphthol is also produced. To separate these three compounds, the mixture is crystallised from alcohol, when the diacetyl derivative is obtained; the alcoholic mother liquor is then poured into water, when ethenylamidonaphthol separates as an oil, whilst acetamido- β -naphthol remains in solution. A mixture of acetamido- β -naphthol and ethenylamidonaphthol is formed by heating 2:1-amidonaphthol hydrochloride with glacial acetic acid and anhydrous sodium acetate for some hours. The relative amount of these compounds varies according to the duration of heating; by half an hour's heating, for example, the product is almost exclusively acetamido- β -naphthol, but after 3—4 hours' heating, ethenylamidonaphthol preponderates. A. R. L.

Methylnaphthalenes. By G. WENDT (*J. pr. Chem.* [2], 46, 317—327).—To separate the α - and β -methylnaphthalenes from each other, the mixture obtained from creosote oil (Schulze, *Abstr.*, 1884, 1183) is cooled until it solidifies, the temperature is then very gradually raised, and the α -methylnaphthalene melted out; this fractional fusion is repeated until the physical constants of the more fusible portion no longer vary (compare Wichelhaus, *Abstr.*, 1892, 492). The proportion of α - to β -methylnaphthalene obtained from the oil by this process was 5:2; Schulze (*loc. cit.*) gives the proportion as 2:3.

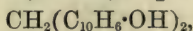
α -Methylnaphthalene is a pale-yellow, mobile oil, stable in air and light; it melts at -22° , and boils at $240-243^{\circ}$ (759 mm., mercury column in vapour); its sp. gr. is 1.0005 at 19° . It dissolves in alcohol and ether, but only very slightly in water; it is volatile with steam, a good solvent, a bad conductor of heat, strongly refractive, and non-fluorescent (compare Wichelhaus, *loc. cit.*). It burns with a luminous flame, has a naphthalene-like odour, and a burning, soapy taste.

β -Methylnaphthalene crystallises in transparent laminæ, melts at 32.5° , boils at $241-242^{\circ}$ (mercury column in vapour; 759 mm.), and dissolves in most of the usual solvents.

Each methylnaphthalene yields two monosulphonic acids, which can be separated by means of their barium salts, one of which is about six times as soluble as the other. The barium α -methylnaphthalene-sulphonates are about twice as soluble as the β -methylnaphthalene-sulphonates. The lead, potassium, and sodium salts were also isolated. In conclusion, the author criticises Wichelhaus (*loc. cit.*).

A. G. B.

Condensation of Formaldehyde with Naphthols. By J. ABEL (*Ber.*, 25, 3477—3484).—*Di- β -naphtholmethane*,



is obtained by the action of methylene dimethyl ether and fuming hydrochloric acid on β -naphthol. Formaldehyde may be used instead of methylene dimethyl ether. It is easily soluble in dilute alkalis, and is precipitated unchanged by acids. It crystallises in long, silky needles, is not volatile with steam, reddens and sinters at 180° , and melts at $188-189^{\circ}$. It does not give the characteristic colour reactions of β -naphthol. The *picrate* melts at $178-179^{\circ}$. The *acetyl derivative*, $\text{CH}_2(\text{C}_{10}\text{H}_6\cdot\text{OAc})_2$, crystallises in slender, lustrous needles, and melts at $212-213^{\circ}$. The *benzoyl derivative*, $\text{CH}_2(\text{C}_{10}\text{H}_6\cdot\text{OBz})_2$, crystallises in slender needles, and melts at $158-159^{\circ}$. The *phenylsulphonate*, $\text{CH}_2(\text{C}_{10}\text{H}_6\cdot\text{O}\cdot\text{SO}_2\text{Ph})_2$, is obtained by shaking phenyl sulphochloride with a solution of the dinaphtholmethane in aqueous soda. It crystallises in beautiful, colourless, strongly-refractive prisms, and melts at 175° . The *dinitroso-compound*, $\text{CH}_2(\text{C}_{10}\text{H}_5\cdot\text{NOH})_2$, is obtained by adding sodium nitrite to a boiling alcoholic solution of the dinaphtholmethane and zinc chloride. It crystallises in brown, lustrous leaflets, is precipitated from its salts by acids in small, yellow needles, containing water of crystallisation, melts at 106° with decomposition, dissolves in alkalis with a green coloration, and closely resembles nitrosonaphthol.

Dibenzeneazodi- β -naphtholmethane, $\text{CH}_2[\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{N}_2\text{Ph}]_2$, is obtained by diazotising a mixture of dinaphtholmethane and aniline hydrochloride, and then adding alkali. It crystallises in beautiful needles, having a green lustre, melts at $127-128^{\circ}$, and is soluble in most organic solvents, but insoluble in alkalis. With concentrated sulphuric acid, it yields a magenta solution, and is precipitated unchanged by the addition of water. With concentrated hydrochloric acid, it yields a beautiful red solution.

Diketodinaphthylmethane, $\text{CH}_2<\begin{smallmatrix} \text{C}_{10}\text{H}_6\text{O} \\ \text{C}_{10}\text{H}_6\text{O} \end{smallmatrix}$, is obtained by treating

β -dinaphtholmethane, dissolved in alkali, with chlorine or bromine water, or with iodine dissolved in potassium iodide. It crystallises in lustrous, sulphur-yellow leaflets, and melts at 168—169°. When reduced with zinc-dust and acetic acid, it is converted into di- β -naphtholmethane. When treated with excess of hydroxylamine hydrochloride, it yields the compound $C_{10}H_6 < \begin{smallmatrix} N \cdot O \\ | \\ CH \end{smallmatrix} > C_{10}H_6$. This is inso-

luble in potassium hydroxide and hydrochloric acid, sparingly soluble in most organic solvents, gives a beautiful red solution with concentrated sulphuric acid, and melts at a high temperature.

Di- α -naphtholmethane is obtained in a similar way to the β -compound as a bright oil, which, after washing with water, forms a hard, brown mass. It dissolves in dilute soda with a beautiful blue coloration, and is precipitated in brown flocks by acids.

Similar condensation products were also obtained from thymol and guaiacol.

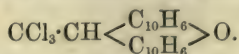
E. C. R.

Condensation of Chloral Hydrate with Naphthols. By A. RUSANOFF (*J. Russ. Chem. Soc.*, **23**, 217—222).—Chloral hydrate (5 grams) and α -naphthol (8.7 grams) are dissolved in acetic acid (15 grams), and to the hot solution is added 1 c.c. of a mixture of equal volumes of acetic and sulphuric acids. When heated on the water-bath, the mixture soon becomes green and turbid, and finally large quantities of crystals separate. These are collected, washed with acetic acid, and dried in a vacuum over sulphuric acid and potash. An analysis of the substance thus obtained corresponded with the formula $CCl_3 \cdot CH(C_{10}H_6 \cdot OH)_2$. The compound crystallises in slender, transparent needles which become grey on keeping; it does not melt, but gradually blackens at 200°. It is easily soluble in ethyl alcohol, methyl alcohol, ether, and acetone, less soluble in acetic acid, and insoluble in benzene and chloroform. The alcoholic solution turns brown on boiling. On heating at 100° with acetic anhydride and sodium acetate, the salt $CCl_3 \cdot CH(C_{10}H_6 \cdot OAc)_2$ is obtained in the solid form; on recrystallisation from acetic acid, it forms shining scales, and melts at 176°.

When β -naphthol is heated with chloral hydrate under the above conditions, no change is observed for a long time. Finally, however, the liquid becomes brown, and gives off hydrogen chloride, a brownish oil separating from which crystals may be obtained. These crystals, on purification, melt at 210° with decomposition. They contain no chlorine, and, on analysis, give numbers corresponding with the formula $C_{22}H_{14}O_3$.

If 10 grams of chloral hydrate and 17 grams of β -naphthol are dissolved in 15 grams of acetic acid, and to the solution there is added gradually, with continued shaking, about 20 c.c. of sulphuric acid, viscous lumps separate, which solidify under water. These are dried, mixed with ethyl acetate and then with alcohol, collected, washed with alcohol, and dried. The substance may be crystallised from chloroform (large tables) or from acetic acid (long needles), but only dissolves with difficulty in these and other solvents. The crystals are

greenish, and the acetic acid solution on heating becomes yellow with a green fluorescence. The formula of the compound is



It does not give the substance $\text{C}_{22}\text{H}_{14}\text{O}_3$ on being heated with sulphuric and acetic acids. Aqueous or alcoholic alkalis do not dissolve it, nor is it attacked by them even on prolonged heating. It dissolves, however, in hot, strong sulphuric acid with evolution of hydrogen chloride.

J. W.

Oxidation of Camphoric acid. By L. BALBIANO (*Real. Accad. Linc.*, 1892, i, 278—284).—On oxidising camphoric acid in alkaline solution with permanganate, an acid of the composition $\text{C}_9\text{H}_{16}\text{O}_6$ is obtained together with oxalic acid; the new acid is a slightly viscid oil, very soluble in water, alcohol, and ether. The calcium salt, $\text{C}_9\text{H}_{14}\text{O}_6\text{Ca}$, forms an amorphous, pulverulent mass readily soluble in water. Both the normal and basic barium salts were prepared; they have the compositions $\text{C}_9\text{H}_{14}\text{O}_6\text{Ba}$ and $4\text{C}_9\text{H}_{14}\text{O}_6\text{Ba}, \text{BaO}$ respectively. The basic lead salt, $2\text{C}_9\text{H}_{14}\text{O}_6\text{Pb}, \text{PbO}$, forms a white powder. The solution of the acid gives no precipitate with copper acetate.

W. J. P.

Action of Hydriodic acid on Piperidine. By E. SPINDLER (*J. Russ. Chem. Soc.*, 23, 39—40).—Hofmann (*Ber.*, 14, 590), by heating pyridine with strong hydriodic acid for a long time at 300° , obtained a hydrocarbon which he judged to be pentane from its boiling point, 35° . Pentamethylene, however, has the same boiling point. The author has therefore again prepared the hydrocarbon obtained by Hofmann. Instead of reducing pyridine, he started from pure piperidine. This substance is not affected by hydriodic acid weaker than sp. gr. 1.96, or at a lower temperature than 300° . On heating with acid of sp. gr. 1.96 at 300° for 10 hours, a hydrocarbon is formed; and this, when washed and dried, distils almost entirely between 33° and 36° , a small quantity remaining which is not volatile at 100° . The sp. gr. of the volatile hydrocarbon is 0.6248 at $17^\circ/17^\circ$; that of normal pentane at the same temperature is 0.6263. As the polymethylenes usually differ considerably in their specific gravity from the saturated hydrocarbons containing the same number of carbon atoms, it seems highly probable that the hydrocarbon from pyridine and from piperidine is actually normal pentane.

J. W.

Action of Piperidine on Haloïd Salts of Mercury. By R. VARET (*Compt. rend.*, 115, 880—881).—Piperidine behaves like pyridine and ammonia towards mercuric halides, molecular compounds containing 2 mols. of base to 1 of halide being formed. It decomposes mercurous halides into mercury and mercuric halides, and then unites with the latter.

Piperidine mercuriochloride, $2\text{C}_5\text{NH}_{11}, \text{HgCl}_2$, made by the direct union of its proximate constituents, crystallises in white, silky tufts of slender needles. It is unstable in the presence of light and air,

and is decomposed by heat, mercury being set free. The *mercurobromide* resembles the mercuriochloride, and is prepared in a similar way. It is decomposed by cold water. The *mercuriocyanide* crystallises in slender needles, and melts at about 85° . It has less tendency to reduction, and is soluble in cold water without decomposition. The *mercuriodide*, which also forms white crystals, is more stable than the chloride, but deposits mercury on boiling. JN. W.

New Collidine. By F. AUERBACH (*Ber.*, 25, 3485—3490).—Aldehyde-collidine (b. p. $174-178^{\circ}$), prepared from aldehyde-ammonia and paraldehyde, when oxidised with 2 per cent. potassium permanganate, yields 6-methylnicotinic acid and isocinchomeronic acid and also small quantities of a methylpyridinedicarboxylic acid and an isomeride of the latter. The methylpyridinedicarboxylic acid, $C_5NH_2Me(COOH)_2 + 2H_2O$, crystallises in beautiful white needles, melts at 158° , and loses 1 mol. H_2O at 100° , and the remaining molecule at a higher temperature with partial decomposition. The isomeric acid melts at 178° , but on account of its great solubility has not yet been obtained pure. The formation of these two acids is contrary to the view that collidine is a 2:5-methyl-ethylpyridine, and by fractional crystallisation of the double salt of collidine with mercuric chloride, the author has isolated a second base from aldehyde-collidine.

Collidine hydrochloride, when treated with a large excess of mercuric chloride, yields a sparingly soluble double salt of the formula $C_8NH_{11},HCl,6HgCl_2$, a salt of the formula $2(C_8NH_{11},HCl),5HgCl_2$, both derived from the same base, and a salt of a second base of the formula $2(C_8NH_{11},HCl),7HgCl_2$.

The salt $C_8NH_{11},HCl,6HgCl_2$ crystallises from hot water in beautiful, rhombic tablets, melts at 168° , and is easily soluble in hydrochloric acid. When allowed to remain some time in a damp state, it is converted into the salt $2(C_8NH_{11},HCl),5HgCl_2$. The latter forms silky needles, and melts at 64° . Pure aldehyde-collidine obtained from these salts boils at $173-174^{\circ}$ (uncorr.), and has a sp. gr. at $0^{\circ} = 0.9369$; at $23^{\circ} = 0.9184$. The platinochloride, which is crystallographically identical with the salt prepared by Ader and Baeyer (*Annalen*, 155, 294), crystallises in orange-red prisms, and melts at 182° . The aurochloride crystallises in golden-yellow needles or transparent tablets, and melts at 87° . The picrate melts at 164° , and crystallises in lustrous leaflets.

The salt $2(C_8NH_{11},HCl),7HgCl_2$, obtained from the mother liquors of the preceding salt, crystallises in aggregates of beautiful prisms, and melts at 116° . The new base obtained from it boils at 177° (uncorr.), and constitutes about 5—10 per cent. of the crude collidine. It is somewhat soluble in water, and has an odour different from that of aldehyde-collidine. The hydrochloride forms hygroscopic needles. The platinochloride, $(C_8NH_{11})_2,H_2PtCl_6$, crystallises in orange-red tablets, and melts at 183° with evolution of gas. The aurochloride crystallises from dilute solutions in spangles, and melts at 115° . The picrate crystallises in needles, and melts at 123° . E. C. R.

Pipecolinecarboxylic acid. By F. AUERBACH (*Ber.*, 25, 3490—3493).—The author has prepared the acids α' -methylnicotinic acid and isocinchomeronic acid, and examined the products obtained by reducing them with sodium and absolute amyl alcohol.

2 : 5-Pipecolinecarboxylic acid, $C_7NH_{13}O_3 + \frac{1}{2}H_2O$, is obtained by the reduction of α' -methylnicotinic acid. It melts at 239° when heated in a closed capillary tube, loses its water of crystallisation at 100° , is very hygroscopic, is a very feeble acid, and has basic properties. The *nitroso-compound* is a pale yellow oil. The *hydrochloride* crystallises in large, transparent prisms, and melts at 221 — 222° . The *platinochloride* is usually obtained as a syrup, but sometimes in beautiful crystals containing water of crystallisation, which it loses at 100 — 110° ; it melts at 199° with decomposition. The *aurochloride* separates in compact crystals, and melts at 185° ; its neutral solution decomposes in the cold, and very quickly on boiling, with precipitation of gold and evolution of carbonic anhydride.

By the reduction of isocinchomeronic acid, a small quantity of a *hydrochloride* crystallising in white needles and melting at 235° was obtained.

E. C. R.

Action of Nascent Hydrogen on Quinolinic acid. By A. PERLMUTTER (*Monatsh.*, 13, 840—850).—Following up the analogous work of Wiedel (this vol., i, 114), the author has studied the action of sodium amalgam on an aqueous solution of sodium quinolinate at 90 — 100° . Reaction occurred much less readily than with most of the analogous acids examined by Wiedel, and only in the presence of much free alkali; the nitrogen of the pyridine ring was eliminated as ammonia and the lactone of $\alpha\gamma\delta$ -butenyl- δ -hydroxytricarboxylic acid, $CH_2 \cdot CH_2 \cdot CH \cdot COOH$

$CO—O \cdot CH \cdot COOH$ obtained. This lactone was purified by conversion into the ethereal salt by means of alcohol and sulphuric acid. The free *lactonic acid* forms a thick syrup, easily soluble in water, alcohol, ethyl acetate, and acetone. The *ethyl salt*, $C_7H_6O_6Et_2$, forms a colourless, thick liquid, almost insoluble in and heavier than water, and having a slight, fruity odour; it cannot be distilled. When an aqueous solution of the lactonic acid is neutralised at 100° with barium carbonate, a *barium salt*, $BaC_7H_6O_6$, is formed. This is easily soluble in water, and the crystals contain water of crystallisation. When a weak solution of this salt is digested with baryta water, *barium hydroxybutenyltricarboxylate*, $Ba_3(C_7H_7O_7)_2$, is formed yielding hairy crystals. Treated with concentrated hydriodic acid, the lactonic acid yields adipic acid, and possibly α -methylglutaric acid. In purifying the adipic acid from ethyl acetate, the author obtained a compound of adipic acid and ethyl acetate, $3C_7H_{10}O_6 + CH_3 \cdot COOEt$, crystallising in small, colourless needles.

Amongst the products of the action of sodium amalgam on quinolinic acid, small quantities of a second acid were present; this is possibly the aldehydic acid, $CHO \cdot CH_2 \cdot CH_2 \cdot CH(COOH) \cdot CO \cdot COOH$.

L. T. T.

Constitution of the so-called Quinoline Ammonium Bases. By W. ROSER (*Annalen*, **272**, 221—229).—Numerous observations have led the author to conclude that the peculiar behaviour of the so-called quinoline ammonium bases must be ascribed to their ready conversion into aldehyde or ketone derivatives; quinoline methochloride, for example, may be assumed to readily undergo change into methylamidocinnamaldehyde, $\text{NHMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CHO}$, in which case its conversion into methylcarbostyryl, a reaction first observed by Decker, would be easily explained.

This view of the behaviour of the quinoline ammonium compounds derives its chief support from the fact that they undergo changes very similar to those observed in the cases of hydrastinine and cotarnine.

Attempts to isolate the above-mentioned hypothetical intermediate products have hitherto been unsuccessful. F. S. K.

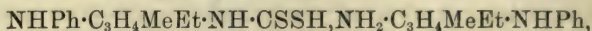
Action of Benzaldehyde on the Ammoniacal Derivative of Dehydrodiacetyllevulinic acid. By G. MAGNANINI and M. SCHEIDT (*Real. Accad. Linc.*, 1892, i, 253—255).—The substance of the composition $\text{C}_8\text{H}_{11}\text{NO}$, which Magnanini obtained (*Abstr.*, 1890, 864) by the action of ammonia on dehydrodiacetyllevulinic acid, yields a condensation product $\text{C}_{15}\text{H}_{15}\text{NO}$ when heated with benzaldehyde and concentrated potash. This compound is readily soluble in alcohol and chloroform, less so in acetic acid, and insoluble in water; it separates from chloroform in small, yellow octahedra which melt at 208.5° , and belong to the orthorhombic system, $a : b : c = 2.3333 : 1 : 1.9301$. Its molecular weight determined by the cryoscopic method in acetic acid solution is normal.

On distilling the compound $\text{C}_8\text{H}_{11}\text{NO}$ with zinc dust, an oil is obtained, which is, doubtless, a homologue of pyrroline. This and other derivatives of the substance are now being investigated.

W. J. P.

Reduction of 1 : 4 : 5-Phenylmethylethylpyrazole and 1 : 3 : 5-Phenyldimethylpyrazole. By G. MARCHETTI (*Real. Accad. Linc.*, **7**, ii, 372—377, and *Gazzetta*, **22**, ii, 368—375).—A boiling solution of 1 : 4 : 5-phenylmethylethylpyrazole in absolute alcohol is reduced by slowly adding small pieces of sodium; water is added, the greater part of the alcohol distilled off, and the solution extracted with ether. The ethereal extract is washed with dilute oxalic acid, the ether distilled off, and the residue again reduced; after 10 repetitions of this process, the oxalic acid washings are united and concentrated, rendered alkaline, and repeatedly extracted with ether. The ethereal solution, on evaporation to dryness, yields an oil which rapidly absorbs carbonic anhydride from the air, and boils at $130\text{--}160^\circ$, in a vacuum, yielding an almost colourless liquid distillate of *methylethylphenyltrimethylenediamine*, $\text{NHPh} \cdot \text{CHEt} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{NH}_2$. The yield is not increased by using amyl alcohol in place of ethyl alcohol. The base has a nauseating odour, is soluble in alcohol and ether, but only very sparingly so in water; it gives the reactions of a primary amine. The *oxalate* separates from anhydrous alcoholic ether in

small crystals, but is rapidly turned brown by atmospheric moisture. Crystalline salts could not be obtained with sulphuric, picric, uric, or succinic acids; the solution in hydrochloric acid reduces platinic or auric chlorides in the cold. The *benzoyl* derivative is a viscid oil, which, on distillation in a vacuum, yields an oil and a crystalline substance. On suspending the base in water and shaking with carbon bisulphide, evaporating off the latter on the water-bath, and adding alcohol until a clear solution is obtained, *methylethylphenyltrimethylenediamine methylethyltrimethyleneanilthiocarbamate*,



is formed, and separates, on cooling, in small needles. It decomposes at 167—170°.

Ether extracts 1 : 3 : 5-phenyldimethylpyrazole from aqueous solutions of its sulphate and oxalate. This pyrazole can be reduced in the same way as the preceding one; on distilling the ethereal extract of the alkaline solution, unaltered dimethylphenylpyrazole is obtained mixed with crystals of 3 : 5-dimethylpyrazole. The latter is extracted with hot water, and, on cooling, separates in beautiful laminæ; the yield corresponds with 10 per cent. of the pyrazole employed. Benzene is also found in the alcohol used in the reduction. The reaction is, therefore, represented by the equation $\text{C}_3\text{N}_2\text{HMe}_2 \cdot \text{C}_6\text{H}_5 + \text{H}_2 = \text{C}_3\text{N}_2\text{H}_2\text{Me}_2 + \text{C}_6\text{H}_6$.

3 : 5-Dimethylpyrazole is soluble in hot water, alcohol, or ether, melts at 106—107°, and boils at 218° under 758·5 mm. pressure. The *silver* compound, $\text{C}_5\text{H}_7\text{N}_2\text{Ag}$, forms a curdy, white precipitate which is not affected by light. The *hydrochloride* is obtained in beautiful, white needles, and is very soluble in water; the *picrate* forms yellow needles. The *platinochloride* crystallises in reddish laminæ or flattened prisms containing 2 mols. of water of crystallisation. It decomposes at 200°, but if kept for some hours at 180—200°, it loses 4 mols. of hydrogen chloride, yielding a red *platinum* compound, insoluble in water. Dimethylpyrazole is oxidised by potassium permanganate, yielding a white, crystalline compound, probably the anhydride of the corresponding dicarboxylic acid. The author is continuing the investigation.

W. J. P.

Reduction of 1 : 3 : 5-Phenyldimethylpyrazole. By G. MARCHETTI (*Real. Accad. Linc.*, 1892, i, 86—92, and *Gazzetta*, 22, ii, 351—359).—The reduction of 1 : 3 : 5-phenyldimethylpyrazole yields 1 : 3 : 5-tetrahydrophenyldimethylpyrazole, in addition to benzene and dimethylpyrazole (compare preceding abstract). The new base is an oil of penetrating, nauseous odour, and boils at 259—260·5° under 758·5 mm. pressure; its sp. gr. at 0°/0° = 1·018. It does not give the pyrazoline reaction with potassium dichromate and sulphuric acid, and yields well crystallised salts. The *platinochloride*, $(\text{C}_{11}\text{H}_{16}\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$, forms a crystalline precipitate, sparingly soluble in cold water; it melts at 177° with decomposition, but loses hydrogen chloride at 140°, yielding a substance insoluble in water. The action of nitrous acid on the base yields the *nitrate*, $\text{C}_{11}\text{H}_{16}\text{N}_2 \cdot \text{HNO}_3$, which forms thin prisms and melts at 113°; no nitroso-derivative could be prepared. The base is oxid-

ised by permanganate solution in the cold, being converted quantitatively into dimethylpyrazole and adipic acid. W. J. P.

Constitution of Acetyl-1-phenylpyrazole. By O. SEVERINI (*Real. Accad. Linc.*, 7, ii, 377—382).—1-Phenylbromacetylpyrazole is formed, with evolution of heat, on adding a solution of bromine in glacial acetic acid to 1-phenylacetylpyrazole dissolved in glacial acetic acid. The mixture is allowed to remain 24 hours at the ordinary temperature, or heated on the water-bath for a few minutes. On adding water, the bromo-derivative separates, and is crystallised first from boiling 30 per cent. alcohol, and then from 95 per cent. alcohol; 85 per cent. of the theoretical yield is obtained. It crystallises in white, silky needles, melts at 131—132°, is soluble in ether or hot dilute alcohol, and very sparingly soluble in cold water. On suspending it in water rendered alkaline by aqueous soda, slowly adding potassium permanganate solution, and heating the liquid at 60—70° on the water-bath, oxidation occurs. The solution is concentrated, acidified with sulphuric acid, and extracted with ether; on evaporation, the ethereal solution deposits a ketonic acid, $C_3N_2H_2Ph \cdot CO \cdot COOH$, which separates from dilute alcohol in lustrous needles; it melts at 168° with decomposition, and is soluble in ether. This acid, when dissolved in very dilute caustic potash and oxidised with potassium permanganate solution, yields 1 : 4-phenylpyrazolecarboxylic acid. Phenylacetylpyrazole is therefore a 1 : 4-derivative.

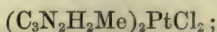
1 : 4-Phenylbromopyrazole does not react with acetic chloride at 280° in a closed tube; the tube exploded at 300—310°. No action occurs with acetic anhydride and sodium acetate at 150—170°.

W. J. P.

Pyrazole Derivatives. By G. MARCHETTI (*Real. Accad. Linc.*, 1892, i, 356—362, and *Gazzetta*, 22, ii, 359—367; compare preceding abstract).—3 : 5-Pyrazoledicarboxylic acid, $C_3N_2H_2(COOH)_2 \cdot H_2O$, is obtained by oxidising the corresponding dimethylpyrazole with potassium permanganate, and crystallises from water in beautiful needles which lose their water of crystallisation at 120°. The anhydrous acid melts at 180° with evolution of carbonic anhydride, and, on distilling it at 280°, pyrazole is obtained. It is soluble in hot water, but only sparingly so in alcohol or ether. The barium salt, $C_3N_2H_2(COO)_2Ba \cdot H_2O$, forms a white, crystalline powder.

3 : 5-Methylpyrazolecarboxylic acid, $C_3N_2H_2Me \cdot COOH$, remains in the mother liquors obtained in the preparation of the preceding acid; it forms small, yellowish crystals, and melts at 235—236° with loss of carbonic anhydride. It is very soluble in hot water, sparingly so in alcohol or ether. The calcium salt crystallises in transparent needles or prisms containing 3 mols. H_2O , which are lost at 120°. On distilling the acid, methylpyrazole, $C_3N_2H_3Me$, is obtained as a heavy, colourless liquid boiling at 200° under 747.5 mm. pressure; it does not solidify at -16°, and is very soluble in all the solvents. The picrate forms small needles melting at 142°, and is very soluble in water. The platinumchloride, $(C_3N_2H_3Me)_2 \cdot H_2PtCl_6 \cdot 2H_2O$, loses its water of crystallisation in a vacuum, and melts with decomposition at

181°. It is very soluble in water, and loses 4 mols. of hydrogen chloride at 235°, leaving a substance of the composition



this compound gives only traces of platinum tetrachloride when dissolved in dilute aqua regia. W. J. P.

Pyrazolone. By R. v. ROTTENBURG (*Ber.*, 25, 3441—3444).—Since v. Pechmann has shown (*Abstr.*, 1892, 816) that the so-called ethyl formylacetate is ethyl β -hydroxyacrylate, it seemed likely that this compound would yield pyrazolone or isopyrazolone on treatment with hydrazine hydrate. Experiment proved, however, that the product of this action is *trimesic trihydrazide*, $\text{C}_9\text{H}_{12}\text{N}_6\text{O}_3$, a compound crystallising from absolute alcohol in large leaves and melting at 100° with decomposition.

The discovery of Wislicenus (*Ber.*, 19, 3225; 20, 3392), that ethyl oxalacetate yields ethyl phenylpyrazolone-3-carboxylate on treatment with phenylhydrazine, suggested that ethyl pyrazolone-3-carboxylate might be obtained by employing hydrazine hydrate instead of phenylhydrazine. As a matter of fact, this is the case, and the two compounds react energetically, but hydrazine acetate and ethyl oxalacetate only react when heated together, with, however, the formation of ethyl pyrazolone-3-carboxylate and the hydrazide of pyrazolone-3-carboxylic acid.

Ethyl pyrazolone-3-carboxylate, $\text{COOEt} \cdot \text{C} \begin{smallmatrix} \text{N} - \text{NH} \\ | \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix}$, crystallises in colourless needles, melts at 179°, forms a blood-red *isonitroso-derivative* and a red *azo-compound*. *Pyrazolone-3-carboxylic hydrazide*,

$\text{NH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{C} \begin{smallmatrix} \text{N} - \text{NH} \\ | \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix}$, forms colourless, flat needles, melts at 238°,

and is readily soluble in water. *Pyrazolone-3-carboxylic acid* is obtained on hydrolysing the ethyl derivative with alkalis or concentrated hydrochloric acid; it decomposes above 250°, yields a yellowish-red *isonitroso-derivative*, and a red *azo-compound*. When the basic

calcium salt, $\text{NH} \begin{smallmatrix} \text{N} = \text{C} \cdot \text{COO} \\ | \\ \text{CO} \cdot \text{CH} \cdot \text{Ca} \end{smallmatrix}$, is heated by itself, or when the acid

is heated with soda lime, *pyrazolone*, $\text{CH} \begin{smallmatrix} \text{N} - \text{NH} \\ | \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix}$, distils over. It

is a mobile oil, boils at 77°, has an intense odour of mice, and becomes yellow on exposure to the air; it is readily miscible with water, alcohol, and ether, gives a yellowish-red *isonitroso-derivative* and a blood-red *azo-compound*. Acid oxidising agents, platinic chloride, for example, give rise to a red coloration. A. R. L.

Papaverinic acid. By G. GOLDSCHMIEDT and F. SCHRANZHOFFER (*Monatsh.*, 13, 697—701).—*Papaverinic anhydride*, $\text{C}_{16}\text{H}_{11}\text{NO}_3$, crystallises in small needles, melts at 169—170°, and may be sublimed uncharged; the *methyl* salt, $\text{C}_{17}\text{H}_{15}\text{NO}_7$, a yellow, crystalline powder, which dissolves in boiling water without decomposition, melts at 153°; and the *ethyl* salt, $\text{C}_{18}\text{H}_{17}\text{NO}_7$, crystallises in small, white

needles, and melts at 187—188°. The *silver* and *ammonium* salts of *papaverinamic acid*, $C_6H_3(OMe)_2 \cdot CO \cdot C_5NH_3(CONH_2) \cdot COOH$, are both well characterised. *Anilpapaverinic anilide*, $C_{28}H_{25}N_3O_6$, is an amorphous powder, which commences to sinter at 107° and melts at 119°.

G. T. M.

Laudanine. By G. GOLDSCHMIEDT (*Monatsh.*, **13**, 691—696).—Pure laudanine, $C_{20}H_{25}NO_4$, contrary to Hesse's statement, is optically inactive in alcoholic, as well as in acid, solutions. It crystallises from a mixture of chloroform and alcohol in well-characterised, rhombic prisms [$a : b : c = 0.7846 : 1 : 0.6124$], and contains three methoxyl groups, having the constitution $C_{17}H_{15}N(OMe)_3OH$. On oxidation with potassium permanganate, in alkaline solution, it is converted into *metahemipinic acid*, $C_6H_2(MeO)_2(COOH)_2$ [$1 : 2 : 4 : 5$]. Laudanine is isomeric with tetrahydropapaverine, but is certainly not identical with it.

G. T. M.

Meconinmethyl Phenyl Ketone. By F. v. HEMMELMAYR (*Monatsh.*, **13**, 663—675).—The preparation of this compound from opianic acid and acetophenone has been previously described by Goldschmiedt (compare Abstr., 1892, 179). It has the constitution $CO \cdot C_6H_2(OMe)_2$
 $O-CH \cdot CH_2 \cdot CPhO$, and, when boiled with dilute potash, is resolved into its generators. On heating with phenylhydrazine in sealed tubes at 150—160°, it is converted into the *hydrazone*, $C_{24}H_{22}O_4N_2$, which crystallises from alcohol in needles and melts at 143—144°, or into the *dihydrazone*, $C_{30}H_{28}O_3N_4$, which crystallises from alcohol in yellow masses, sinters at 176°, and is completely molten at 187°. Two oximes, of the formula $C_{18}H_{17}O_5N$, are obtained on heating the ketone with free hydroxylamine in sealed tubes at 150°. Each of these stereoisomerides is almost insoluble in water, and crystallises from alcohol in white needles. They melt at 146° and 198° respectively.

G. T. M.

Cinchona Alkaloids, particularly Quinine. By A. CLAUS (*J. pr. Chem.* [2], **46**, 336—351).—This is a polemical paper, dealing with Grimaux's paper on quinine methiodides (Abstr., 1892, 1363).

Molecular Transformation of Cinchonine. By G. PUM (*Monatsh.*, **13**, 676—690; compare Abstr., 1892, 514; Lippmann and Fleissner, *ibid.*, 81; and Skraup, *ibid.*, 83).—The author has repeated, on a larger scale, the investigation of the products formed by decomposing trihydriodicinchonine with alcoholic potash and with silver nitrate respectively. He finds that in the first case cinchonine and isocinchonine are produced, whilst in the second, isocinchonine and *β*-cinchonine result from the decomposition.

β-Cinchonine melts at 250—252°, and forms a trihydriodo-derivative, $C_{19}H_{22}N_2O \cdot 3HI$, which melts at 228—229°, and is resolved by potash or silver nitrate into *β*-cinchonine and a small quantity of isocinchonine.

Trihydriodoisocinchonine, $C_{19}H_{22}N_2O \cdot 3HI$, melts at 227—229°, and is converted by alcoholic ammonia into dihydriodoisocinchonine, $C_{19}H_{22}N_2O \cdot 2HI$, which melts at 192—193°. When heated with

alcoholic potash, it is resolved into a mixture of isocinchonine and γ -cinchonine. The latter crystallises from absolute alcohol in small, transparent needles, melts at $235-236^\circ$, and forms an anhydrous, crystalline platinochloride.

β -Cinchonine and γ -cinchonine, or one of them, is, in all probability, identical with the optically active isomeride or isomerides of cinchonine isolated by Jungfleisch and Leger. G. T. M.

Coca Leaves. By C. LIEBERMANN (*Annalen*, **272**, 238—242).—A polemical paper in reply to Hesse (this vol., i, 57).

Geoffroya Barks. By O. HILLER-BOMBIEN (*Arch. Pharm.*, **230**, 513—548).—The barks known under the above name, including cabbage-tree bark and worm bark, were employed medicinally as anthelmintics about the end of the last century, but are now practically obsolete.

Hüttenschmid, in 1824 (and, later, Overduin and also Winkler), isolated an alkaloid, *surinamine*, or *geoffroyine*, from true *Geoffroya* bark.

Geoffroyine (*methylytyrosine*?), $C_{10}H_{13}NO_3$, occurs in *geoffroya* bark, and is identical with rhatanine obtained by Ruge, in 1854, from rhatany extract, and with angeline, obtained by Gintl, in 1869, from the resin of the *Ferreia spectabilis*. The same alkaloid is also present in various species of andira bark, and the author, therefore, proposes to adopt the name *andirine* in preference to those above given.

The alkaloid is isolated by repeatedly extracting the bark with boiling water and evaporating the combined extracts, when a brown, hygroscopic mass remains. This is treated with hydrochloric acid, the solution filtered from the insoluble impurities, and the filtrate neutralised, when, if the solution be dilute, the alkaloid separates in large, white crystals. This operation is repeated until the compound is pure. It is tasteless, its solution has a neutral reaction and is optically inactive, and, when the compound is allowed to remain with nitric acid (sp. gr. 1.4) for three days, it is converted, for the most part, into picric acid. It is soluble in 200 parts of boiling water, and in 695 parts of cold; also in 15,000 parts of absolute alcohol and in 914 parts of glacial acetic acid, but quite insoluble in benzene, ether, light petroleum, and several other solvents. Heated in a capillary tube, the compound melts at 233° , but its melting point is found to be 257° (corr.) when the determination is made by Dragendorff's method (*Pflanzenanalyse*, 1882, p. 13). The *hydrochloride* and *sulphate* are dissociated by water, and the free base is obtained when the alkaloid is dissolved in glacial acetic acid and the solution evaporated. The *copper salt*, $(C_{10}H_{12}NO_3)_2Cu$, crystallises in anhydrous, microscopic, violet needles, and is sparingly soluble in water; a silver salt could not be prepared, as a solution of the base is reduced by silver oxide. When bromine is added to an aqueous solution of the base, the *dibromide*, $C_{10}H_{11}Br_2NO_3$, separates as a yellow, curdy precipitate, soluble in alcohol, chloroform, and aqueous ammonia. If the alkaloid is boiled with acetic anhydride, an acetyl derivative is formed, but it

remains unaltered when heated in a sealed tube at 80° with methyl iodide.

The alkaloid dissolves in concentrated sulphuric acid, forming a colourless solution which becomes brown on heating; an acid solution of vanadium sulphate gives a violet coloration, and, when the compound is evaporated with nitric acid, the residue gives a brick-red coloration with potassium hydroxide. On mixing the compound with water, and then adding nitric acid drop by drop, until it dissolves, and subsequently heating, a yellowish-red solution is obtained, which changes to bluish-violet, and finally becomes green with a reddish fluorescence. The alkaloid dissolves in Millon's reagent, forming a dark red solution exhibiting an absorption of the spectrum from lines D to H. To detect the alkaloid in a sample of bark, the latter is boiled with water, treated with basic lead acetate, and the filtrate, after removal of the lead, warmed with Millon's reagent, when a red coloration is produced, and subsequently a precipitate.

A. R. L.

Ptomaines from the Urine in Erysipelas and Puerperal Fever. By A. B. GRIFFITHS (*Compt. rend.*, 115, 667—669).—The urine of erysipelas patients yields a ptomaine which crystallises in white lamellæ belonging to the rhombic system; it is soluble in water, and has a feebly alkaline reaction. With mercuric chloride, it yields a flocculent precipitate; with zinc chloride, a granular precipitate, partially soluble with decomposition when heated; with Nessler's reagent, a green precipitate; with picric acid, a yellow precipitate; with gold chloride, a yellow precipitate; and precipitates also with phosphomolybdic, phosphotungstic, and tannic acids. This ptomaine has the composition $C_{11}H_{13}NO_3$, and the author calls it *erysipeline*; it is highly poisonous, and produces high fever, resulting in death in a few hours. It does not occur in normal urine.

The urine of patients suffering from puerperal fever yields a white, crystalline ptomaine of the composition $C_{22}H_{19}NO_2$, which is not found in normal urine. It forms a crystallisable hydrochloride and aurochloride, yields a red precipitate with tannin, a yellow precipitate with picric acid, and a brownish precipitate with phosphomolybdic acid; it is also precipitated by Nessler's solution. This ptomaine is highly poisonous.

C. H. B.

Preparation and Properties of Fibroïn. By L. VIGNON (*Compt. rend.*, 115, 613—615).—The statements of various chemists as to the proportion of fibroïn obtainable from raw silk differ very widely, and the author has therefore reinvestigated the matter.

10 grams of raw silk were boiled for 30 minutes with a solution of 150 grams of neutral white soap in 1500 c.c. of water, well washed, and then boiled for 20 minutes with a second similar quantity of soap solution. After this treatment, it was well washed with water, then with water acidified with hydrochloric acid, again with pure water, and, finally, with alcohol of 90° . In this way, 75 per cent. of fibroïn is obtained as a very brilliant, white, soft, tenacious, and elastic substance of sp. gr. about 1.34. Its percentage composition is C, 48.3;

H, 6.5; N, 19.2; O, 26.0 = 100.0, and it contains only 0.01 per cent. of ash.

When added to hydrochloric acid of 22°, fibroin at first dissolves rapidly, but, as its proportion increases, it forms a viscous, transparent mass, exactly similar to the silk in the gland of the silkworm. A solution in concentrated hydrochloric acid is strongly lævogyrate. Alcohol of 95° precipitates the fibroin from hydrochloric acid solutions in a form closely resembling gelatinous silica, and when dried at the ordinary temperature, it resembles dry albumin. Although it has lost its lustre, it retains its original composition, sp. gr., optical activity, and power of combining with colouring matters.

C. H. B.

Turacin. By A. H. CHURCH (*Proc. Roy. Soc.*, **51**, 399—400).—Turacin, a definite, organic pigment, containing, as an essential constituent, about 7 per cent. of copper, occurs constantly in all the 18 known species of the three genera *Turacus*, *Gallirex*, and *Musophaga*, but is absent from the seven species included in the three remaining genera of the family *Musophagidae*, namely, *Corythæola*, *Schizorhis*, and *Gymnoschizorhis*.

In alkaline solutions, turacin shows an absorption spectrum consisting of the two dark bands previously described (*Phil. Trans.*, **159**, 627—636), and a faint, broad band, λ 496 to λ 475. Isolated turacin in ammoniacal solution shows these three bands and also a fourth, a narrow band extending from λ 605 to λ 589. The last band is probably due to the presence of traces of the green alteration product of turacin, which is probably identical with Krukenberg's *turacoverdin*. The ammoniacal solution remains unchanged, even after so long a period as 23 years.

Dry turacin, when suddenly and strongly heated, yields a volatile red derivative containing copper; it is insoluble in dilute ammonia solution, but dissolves in, and can be crystallised from, ether. When heated at the boiling point of mercury, dry turacin gives off no visible vapour, but is profoundly altered, becomes black, and insoluble in alkaline solutions, and gives off no vapours when strongly heated.

Turacin has the composition C, 53.69; H, 4.60; Cu, 7.01; N, 6.96; O, 27.74; but, although these numbers agree closely with those required by the formula $C_{82}H_{81}Cu_2N_9O_{32}$, the author does not attach very great weight to the results.

In some respects, turacin is analogous to hæmatin, and, when treated with sulphuric acid, it yields a coloured derivative *turacoporphyrin*, the spectra of which, in both acid and alkaline solutions, closely resembles those of hæmatoporphyrin. Turacoporphyrin, however, contains copper, whilst hæmatoporphyrin is free from iron.

C. H. B.

Organic Chemistry.

Graphochemistry of Compounds $C_nH_mO_p$. By E. NICKEL (*Zeit. physikal. Chem.*, 10, 621—637; compare Abstr., 1892, 1158).—If p in the general formula $C_nH_mO_p$ is made equal to unity, and the percentage amounts of carbon and hydrogen are tabulated on rectangular axes, it is easy to define a field within which the composition of all compounds $C_nH_mO_p$ must lie, the limits in the various directions being given by the substances C, CH_4 , CO_2 , CH_3O , $C(OH)_4$, and H_2O . The interpretations of the different lines and pencils of rays obtained in the diagram are interesting, and are fully discussed by the author. Applications are made to the study of the possible decompositions of the substances without extraneous material being involved, and to the relation of composition to vapour density.

J. W.

Carbon Chloriodide. By A. BESSON (*Compt. rend.*, 115, 1078—1079).—Carbon tetrachloride, mixed with its own weight of dry carbon bisulphide, is cooled to 0° , and successive small quantities of iodine are added, care being taken to avoid access of air and to keep the carbon tetrachloride in large excess. After two or three days, the excess of carbon tetrachloride and the carbon bisulphide are distilled off, after treatment with a dilute solution of an alkali. The fraction boiling above 142° is purified by treatment with a solution of an alkali and distillation in a vacuum. The product is *carbon trichloriodide*, CCl_3I , a colourless liquid with an aromatic odour and an irritating vapour; it solidifies at a low temperature, and melts at -19° ; it boils at 142° , with partial decomposition in presence of air or an inert gas, but distils without change in a vacuum; sp. gr. at $17^\circ = 2.36$. In presence of air, or even of an inert gas, it decomposes at the ordinary temperature with separation of iodine and formation of carbon hexachloride, C_2Cl_6 , and the change, which seems to reach a limit after a time, is promoted by exposure to light. In contact with mercury, decomposition is complete after a few hours.

C. H. B.

Reaction between Ferric Salts and Soluble Thiocyanates. By G. KRÜSS and H. MORAHT (*Zeit. anorg. Chem.*, 1, 399—404).—The authors confirm the results obtained by Magnanini (Abstr., 1891, 1150), that in dilute solutions the addition of 12 mols. of a soluble thiocyanate to 1 mol. of a ferric salt does not suffice to convert the whole of the iron into the well-known red compound, and to produce the maximum coloration. In view of their former experiments (Abstr., 1889, 1129), they still regard the reaction as taking place in accordance with the equation $FeCl_3 + 12KCNS = Fe(CNS)_3 + 9KCNS + 3KCl$; but in order to realise the reaction in dilute solution, it is necessary, perhaps owing to electrolytic dissociation, that the thiocyanate should be present in excess.

H. C.

Action of Anhydrous Hydrogen Fluoride on Alcohols. By M. MESLANS (*Compt. rend.*, **115**, 1080—1082).—Anhydrous hydrogen fluoride has no action on absolute alcohol below 130° . At 140° , after six hours, about 2 per cent. of the alcohol is etherified; at 170° , 20 per cent. of the maximum possible change takes place. The best temperature is 210 — 220° , and, by using 4 mols. of the acid to 1 mol. of the alcohol, about 33 per cent. of the alcohol is etherified in three hours, and several litres of gaseous ethyl fluoride can be collected. Propyl and isopropyl alcohols and their homologues, under the same conditions, yield large quantities of the corresponding alkyl fluorides. The reacting substances are heated together in a copper tube, lined with platinum, and fitted with a screw-tap and a delivery tube by means of which the gas can be allowed to escape. C. H. B.

Rotatory Power of Sugars. By I. I. KANONNIKOFF (*J. Russ. Chem. Soc.*, **23**, 367—375).—In general, when two optically active sugars are mixed in molecular proportion, in solution, the specific rotatory power of the mixture is the mean of that of the components. There are exceptions to this rule, however, as the following table shows:—

	[α] _D .	
	Found.	Calculated.
1 mol. dextrose + 1 mol. levulose.	— 9.85°	— 19.97°
1 mol. „ + 2 mols. „	— 44.91	— 44.97
1 mol. „ + 3 mols. „	— 57.29	— 57.41
2 mols. „ + 1 mol. „	+ 9.68	+ 4.99
3 mols. „ + 1 mol. „	+ 17.52	+ 17.47

The author attributes these discrepancies to the mutual action of the components of the mixture. J. W.

Formation of Ethereal Salts of Benzoic acid from Alcohols and Carbohydrates. By A. PANORMOFF (*J. Russ. Chem. Soc.*, **23**, 375—382).—1 part of a polyatomic alcohol or carbohydrate was added to 6 parts of benzoic chloride and 48 parts of an 18—20 per cent. solution of soda. The mixture was shaken for about an hour at 0° , allowed to remain over night, and the precipitate which separated from the liquid was washed with water until it showed an acid reaction. It was then crystallised from 95 per cent. alcohol until the melting point was constant.

The following benzoates were prepared in this way:—

From *dextrose*, $C_6H_7O_6Bz_5$, amorphous, m. p. 178° .

From *levulose*, $C_6H_7O_6Bz_5$, amorphous, m. p. 78 — 79° .

From *galactose*, $C_6H_7O_6Bz_5$, m. p. 78 — 82° .

From *cane sugar*, $C_{12}H_{15}O_{11}Bz_7$, amorphous, m. p. 98° .

From *milk sugar*, $C_{12}H_{16}O_{11}Bz_7$, long crystals, m. p. 200° .

From *maltose*, $C_{12}H_{22}O_{11}Bz_7$, amorphous, m. p. 109—115°.

From *glycogen* (from liver and muscle), $C_6H_5O_5Bz_2$, amorphous, turns brown at 187°, melts at 195°.

From *mannitol*, $C_6H_8O_6Bz_6$, recrystallised from acetic anhydride, fine needles, m. p. 149°. J. W.

Conversion of Starch into Sugar by means of Blood Serum.

By F. RÖHMANN (*Ber.*, 25, 3654—3657).—The author has fully identified the sugar formed by the action of blood serum on potato starch as being dextrose; the yield of the sodium chloride derivative is 40 grams from 110 grams of starch. Maltose appears to be formed at the commencement of the operation. Soluble starch and dextrin are also produced, the quantities depending on the length of time the fermentation is allowed to proceed. The dextrin may be separated into two portions by treatment with methyl alcohol; one of these, achroödextrin, is not acted on by iodine, whilst the other is coloured brown. J. B. T.

Chemical Conditions of the Action of Diastases. By J.

EFFRONT (*Compt. rend.*, 115, 1324—1326).—The saccharifying power of amylase, glycose, and the soluble ferment of *Aspergillus oryzae*, or a mixture of them, can be increased in the proportion of 1 to 10 by the addition of aluminium salts, phosphates, asparagine, and certain albumins. In the case of aluminum acetate, ammonium phosphate, and asparagine, the effect is the same whether the salt is first mixed with the diastase and the starch added, or is mixed with the starch and the diastase added; but with calcium phosphate and with alum, the results differ according to the mode of procedure. The influence of these chemical compounds is independent of the temperature at which saccharification takes place, but decreases as the quantity of sugar increases, and disappears when the proportion of sugar reaches 60 per cent., a result due to the nature of the different dextrins formed during the conversion of starch into sugar.

It is noteworthy that the substances that promote the action of the diastases are also those which promote the action of organised ferments. The action of the salts is probably the same in both cases, and it seems likely that their effect is due to the formation of intermediate compounds, and, consequently, that their mode of action is analogous to that of metallic salts in Friedel and Craft's synthesis.

C. H. B.

Amidoacetaldehyde (Ethanalamine). By E. FISCHER (*Ber.*, 26, 92—98).—*Amidoacetaldehyde hydrochloride* is obtained by adding an aqueous solution of amidoacetal, drop by drop, to well-cooled hydrochloric acid (sp. gr. = 1.19), and after allowing the mixture to remain at the ordinary temperature 4—5 hours, distilling it in a vacuum at 40°. The hydrochloride remains as a colourless syrup, which deliquesces on exposure to air and has not been obtained crystalline. The *hydrobromide* is prepared in the same way and resembles the hydrochloride. The *platinochloride*, $(CHO \cdot CH_2 \cdot NH_2)_2, H_2PtCl_6 + 2C_2H_6O$, is prepared in alcoholic solution; it crystallises in yellow, microscopic needles and decomposes at 80—90°. When prepared in

methyl alcoholic solution, it crystallises in small, six-sided, yellow tablets, containing 2 mols. of methyl alcohol.

Amidoacetaldehyde is so unstable that it has not yet been isolated. When the hydrochloride is warmed with dilute sodium hydroxide, ammonia is evolved; when treated with a cold solution of barium hydroxide, a gelatinous mass is obtained. The alkaline solutions energetically reduce Fehling's solution and ammoniacal silver solutions. The hydrochloride is converted into amidoacetic acid when oxidised with bromine, and into glyoxalphenylosazone when treated with phenylhydrazine acetate.

Glyoxalphenylosazone has been obtained by crystallisation from ether in well-formed crystals, which melt at 177° (179° , corr.) and belong to the monoclinic system, $a : b : c = 0.8638 : 1 : 1.9029$; $\beta = 72^{\circ} 36' 37''$.

E. C. R.

Thiocyanacetone. By J. TOCHERNIAC (*Ber.*, **25**, 3648; compare *Abstr.*, 1892, 1425).—A reply to Hantzsch's criticism (this vol., i, 64) of the author's previous work on this subject.

J. B. T.

Constitution of Isomeric Aliphatic Oximes. By G. MINUNNI (*Gazzetta*, **22**, ii, 431—438).—This paper is a reply to the objections raised by Hantzsch (*Abstr.*, 1892, 1268) and V. Meyer (*Abstr.*, 1892, 992) to the author's explanation of the isomerism of the oximes; no new facts are brought forward.

W. J. P.

Perchlorethyl Chloroformate and Trichloromethyl Trichloroacetate. By R. ANSCHÜTZ and W. O. EMERY (*Annalen*, **273**, 56—63; compare Müller, *Abstr.*, 1890, 1095).—Trichloromethyl trichloroacetate, $\text{CCl}_3\text{COOCCl}_3$, was prepared by chlorinating methyl trichloroacetate at the ordinary temperature, and purified by repeated fractional distillation under reduced pressure; it is a colourless, crystalline compound, melts at 34° , and boils at $73\text{--}74^{\circ}$ under a pressure of 10 mm., and at $191\text{--}192^{\circ}$ under the ordinary atmospheric pressure; its sp. gr. = 1.67331 at $35^{\circ}/4^{\circ}$.

Perchlorethyl chloroformate, $\text{Cl}\cdot\text{COOC}_2\text{Cl}_5$, obtained from ethyl chloroformate in a similar manner, forms transparent crystals, melts at $26\text{--}27^{\circ}$, and boils at $83\text{--}84^{\circ}$ under a pressure of 10 mm., and at $209\text{--}210^{\circ}$ under the ordinary atmospheric pressure; its sp. gr. = 1.73702 at $35^{\circ}/4^{\circ}$.

These facts show that the two compounds are not identical, although, as was observed by Cloez (*Ann. Chim. Phys.* [3], **17**, 297), they are both decomposed by water, yielding hydrogen chloride, carbonic anhydride, and trichloroacetic acid; this identity in behaviour can be explained by assuming that they are both converted into an intermediate product of the constitution $\text{COCl}\cdot\text{O}\cdot\text{CO}\cdot\text{CCl}_3$.

F. S. K.

Brom-additive Products of Angelic and Tiglic acids. By R. FITTIG (*Annalen*, **273**, 127—132).—The author disputes the accuracy of some of Wislicenus' methods (this vol., i, 135) and results, and refuses to continue the discussion of the matters in question.

F. S. K.

New Unsaturated Fatty Acid. By Y. SHIMOYAMA (*Chem. Centr.*, 1892, ii, 646; from *Apoth. Zeit.*, 7, 453—454).—*Senecioic acid*, $C_4H_7\cdot COOH$, occurs in the rhizomes of the Japanese evergreen *Senecio Kämpferi*; it crystallises in odourless, colourless, silky needles or prisms, melts at 65° , and decomposes carbonates. The silver salt forms white, silky plates; the calcium salt, with $3H_2O$, needles, soluble in water. With bromine, in carbon bisulphide-solution, it yields the dibromide, $C_4H_5Br_2O_2$, which forms colourless crystals melting at 107° . By the action of hydrobromic acid, saturated at 0° , it is converted into hydrobromosenecioic acid, $C_4H_5Br\cdot COOH$, which crystallises in colourless needles and melts at 71° . Nascent hydrogen does not act on senecioic acid. A. J. G.

Intramolecular Changes in Unsaturated Acids. By R. FITTIG (*Ber.*, 26, 40—49).—This paper contains a *résumé* of the work carried out on this subject by the author and his pupils, a full account of which will shortly be published.

The author previously observed (*Abstr.*, 1891, 452) that certain $\beta\gamma$ -unsaturated acids are converted by the action of boiling aqueous soda into the isomeric $\alpha\beta$ -acids; a large number of other acids of the first-named class have now been examined, and the same rule has been found to hold good in every case; the conversion is, however, never complete, as the reverse reaction also takes place, and some β -hydroxy-acid is always formed by the union of the unsaturated acid with the elements of water. Hence a condition of equilibrium is eventually reached between the proportions of the three acids, the point of which probably depends on the concentration of the soda solution. The pure hydroxy-acids when treated alone with soda again lose water, and yield a mixture of the $\alpha\beta$ - and $\beta\gamma$ -unsaturated acids, the former being obtained in much larger quantity, and the $\alpha\beta$ -acids themselves under the same conditions are partially converted into the $\beta\gamma$ -acids. Whether all these reactions are caused by the primary formation of the β -hydroxy-acids, or whether the $\alpha\beta$ -acids are first formed and then converted into the hydroxy-acids, is as yet uncertain.

The $\alpha\beta$ -acids are distinguished from the $\beta\gamma$ -acids by their higher melting points, and by the fact that dilute sulphuric acid, which converts the $\beta\gamma$ -acids in a few minutes into the hydroxy-acids, is without action on them; this forms, therefore, a ready and accurate method of separating the members of the two series. The whole of the evidence is against the view that the first series are stereoisomerides of the second; thus both combine with bromine and hydrogen bromide, yielding different dibromides and monobromoderivatives; the latter, when obtained from the $\beta\gamma$ -acids, are readily converted by boiling water into lactones, whilst those from the $\alpha\beta$ -acids yield unsaturated hydrocarbons and hydroxy-acids.

Allylacetic acid, $CH_2\cdot CH\cdot CH_2\cdot CH_2\cdot COOH$, remains unaltered after boiling for several hours with concentrated alkali, whereas the isomeric ethylenepropionic acid, $CH_3\cdot CH\cdot CH\cdot CH_2\cdot COOH$, is converted into an acid which is probably propylenecacetic acid, $CH_3\cdot CH_2\cdot CH\cdot CH\cdot COOH$. Allylmalonic acid is also indifferent towards alkali.

The conversion of the lactonic acids (paraconic acids) into the unsaturated dicarboxylic acids homologous with itaconic, citraconic, and mesaconic acids has also been closely followed in a large number of cases, and the chemical and physical properties of these acids were found to be largely reproduced in their homologues. All the citraconic acids are very readily soluble in water, and melt below or slightly above 100° , splitting up at the same time into anhydride and water; the solubility of the itaconic and mesaconic acids, on the other hand, decreases with an increasing number of carbon atoms. The itaconic acids melt only with simultaneous decomposition, but the mesaconic acids, although possessing the highest melting points, can be melted without decomposition; the latter are identical with the so-called oxytetric and oxypentic acids (compare Abstr., 1891, 1188).

The conversion of the itaconic into the citraconic acids is brought about by dry distillation, some of the itaconic anhydride passing over at the same time, the quantity of the latter being increased if the distillation is carried out in a vacuum. In the case of teraconic acid (dimethylitaconic acid), the itaconic anhydride is then exclusively formed, but at the atmospheric pressure some of the citraconic anhydride is also formed. To separate the citraconic acids, the distillate is boiled with water, when the citraconic anhydride distils over with the water.

Phenylitaconic acid shows a somewhat anomalous behaviour, inasmuch as, even when distilled in a vacuum, it undergoes a far-reaching decomposition; if simply melted in a vacuum, however, a little citraconic anhydride is formed, together with the itaconic anhydride, and may be extracted with carbon bisulphide, in which the latter is insoluble. If it be again heated to its melting point ($160-165^{\circ}$), which is approximately the same as the temperature at which it is formed, it is reconverted almost completely into the itaconic anhydride.

The conversion of the citraconic into the mesaconic acids is best brought about by the action of a small quantity of bromine on a chloroform solution in bright daylight or sunlight; the change takes place in a few minutes, the mesaconic acid separating out in crystals, which, after washing with chloroform, are pure. This method is also the most suitable for the preparation of mesaconic acid itself from citraconic acid, with the modification that the latter is dissolved in ether. That the hydrogen bromide formed in the reaction is not the agent which effects the change, is shown by the fact that hydrogen bromide alone is incapable of bringing it about, and the explanation given by Wislicenus for this change is, therefore, no longer tenable. In absence of light and water, bromine acts only very slowly on citraconic acid, the chief product being then citradibromopyrotartaric acid.

The itaconic acids are only attacked with difficulty by nascent hydrogen, the mesaconic acids more readily, and the citraconic acids the most easily; in all cases the same succinic acid is obtained from all three isomerides. When heated with concentrated hydrochloric or hydrobromic acid, and subsequently boiled with water, the itaconic acids are converted into the paraconic acids from which they were obtained, except in the case of isopropylitaconic acid, which, in place

of the original isopropylparaconic acid, $\text{COOH} \cdot \text{CH} - \text{CH}_2$
 $\text{CHPr}^s \cdot \text{O} > \text{CO}$, yields
 an isomeric lactonic acid, which has probably the constitutional
 formula $\text{CMe}_2 \cdot \text{CH}_2$
 $\text{O} - \text{CO} > \text{CH} \cdot \text{CH}_2 \cdot \text{COOH}$, as it is also obtained by oxidising
 isobutylsuccinic acid with alkaline permanganate. The change is
 similar to that which takes place in preparing tertiary butyl alcohol
 from isobutyl alcohol.

The itaconic acids are not altered by boiling with soda, except in so
 far as a small quantity of hydroxy-acid is formed, whilst the citra-
 conic and mesaconic acids are converted into the itaconic acids, the
 former more quickly than the latter. In no case was the formation
 of citraconic acids from either of the other two series observed.
 According to Delisle (Abstr., 1892, 297), citraconic acid is under
 these conditions converted into mesaconic acid, and the author has
 confirmed this statement; the exception is not due to the abnormal
 behaviour of citraconic acid, for this is converted as usual into ita-
 conic acid; the latter is, however, itself converted by boiling soda
 into mesaconic acid.

H. G. C.

Diglycollic acid and Thiodiglycollic acid. By R. ANSCHÜTZ
 and F. BIERNAX (Annalen, 273, 64—73; compare Abstr., 1891, 177).
 —*Diglycollic chloride*, $\text{O}(\text{CH}_2 \cdot \text{COCl})_2$, is formed when diglycollic acid
 is treated with phosphorus pentachloride (2 mols.); it is a colour-
 less, oily, highly-refractive liquid, boils at 116° under a pressure of
 about 12 mm., and is immediately decomposed by water.

Methyl diglycollate, $\text{O}(\text{CH}_2 \cdot \text{COOMe})_2$, prepared by treating the
 chloride with methyl alcohol, crystallises in lustrous, colourless plates,
 and melts at 36° .

Diglycollanil, $\text{O} < \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} > \text{NPh}$, is obtained when diglycollanilic
 acid (*loc. cit.*) is treated with excess of acetic chloride; it crystallises
 in small prisms melting at 111° .

Diglycollanilide, $\text{O}(\text{CH}_2 \cdot \text{CO} \cdot \text{NHPh})_2$, prepared by treating a well-
 cooled ethereal solution of the chloride with aniline, crystallises in
 colourless needles, and melts at 152° .

Thiodiglycollic anhydride, $\text{S} < \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} > \text{O}$, is produced when the
 acid is boiled with acetic chloride, or distilled under reduced pres-
 sure; it crystallises in colourless needles, melts at 102° , and boils at
 153° , under a pressure of about 10 mm.; it is very readily decom-
 posed by water. The *chloride* $\text{S}(\text{CH}_2 \cdot \text{COCl})_2$ was prepared.

Methyl thiodiglycollate, $\text{S}(\text{CH}_2 \cdot \text{COOMe})_2$, is a colourless, highly
 refractive liquid, boiling at 135° , under a pressure of about 11 mm.

Thiodiglycollanilic acid, $\text{NHPh} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COOH}$, separates
 from boiling water in well-defined crystals melting at 103° .

Thiodiglycollparatolilic acid, $\text{C}_{11}\text{H}_{13}\text{SNO}_3$, crystallises in colourless
 needles, and melts at 95° .

Thiodiglycollanilide, $\text{S}(\text{CH}_2 \cdot \text{CO} \cdot \text{NHPh})_2$, crystallises in needles
 melting at 168° .

F. S. K.

Action of Water on Bromosuccinic acid. By S. TANATAR (*J. Russ. Chem. Soc.*, **23**, 339—343).—When a solution of bromosuccinic acid is allowed to remain at the ordinary temperature, no change takes place, but a solution of its potassium salt undergoes considerable decomposition in 24 hours under the same circumstances. The amount of decomposition was measured by the author by the increase in the acid titre of the solution, consequent on the formation of hydrobromic acid. When the acid or its potassium salt is heated at 100°, decomposition takes place, and is practically complete within 12 hours. The more dilute the solution, the more rapid is the decomposition. Hydrochloric acid does not greatly influence the speed of the reaction. The products of the action of water on bromosuccinic acid are inactive lactic acid and hydrobromic acid, fumaric acid not being formed, at least primarily. J. W.

Mixed Anhydrides of Hypochlorous and Analogous Acids. By T. SELIVANOFF (*Ber.*, **25**, 3617—3623).—The author proposes that chlorine, when present in a compound as the radicle of hypochlorous acid, be termed *chloryl*; thus he names the compound $\text{Ac}\cdot\text{NHCl}$, chlorylacetamide.

Chlorylsuccinimide, $\begin{array}{c} \text{CH}_2\cdot\text{CO} \\ | \\ \text{CH}_2\cdot\text{CO} \end{array} > \text{NCl}$, is obtained by the action of hypochlorous acid on succinimide. It is a powerful oxidising agent. Primary and secondary alcohols are oxidised, but trimethylcarbinol is not attacked; it may be employed, therefore, to ascertain whether a given alcohol is tertiary or not. The presence of water is necessary to develop the oxidising powers of chlorylsuccinimide; thus a solution of chlorylsuccinimide in dry benzene is without action on potassium iodide, but if the smallest quantity of water is added, iodine is at once liberated; the imide is decomposed by warm water into succinimide and hypochlorous acid, the aqueous solution showing all the properties of hypochlorous acid. From these results, the author concludes that chlorylsuccinimide is an anhydride or amide of hypochlorous acid. Other similar acid amides containing chlorine, which the author has examined, behave like chlorylsuccinimide, and are considered to be anhydrides of hypochlorous acid.

The chlorine derivatives of amines, $\text{R}\cdot\text{NHCl}$ and RNCl_2 , behave in a manner analogous to the derivatives of the acid amines, and when hydrolysed with dilute sulphuric acid yield hypochlorous acid; they also have chlorinating and oxidising properties. Thus, dichlorylethylamide, EtNCl_2 , when treated with water, yields 2 mols. HClO .

Succinimide, when treated with chlorylacetamide, yields chlorylsuccinimide, which is an anhydride of hypochlorous acid, and, therefore, chlorylacetamide must be a similar anhydride. In this way, by acting on amines with chlorylacetamide or chlorylsuccinimide, the author has obtained the following compounds:—Dichlorylethylamide, chloryldiethylamide, chlorylpiperidine, $\text{C}_5\text{H}_{10}\text{NCl}$, chloryldipropylamide, and chloryldiisobutylamide. E. C. R.

Condensation of Ethyl Formate and Succinate. By F. ANDERLINI and E. BORISI (*Gazzetta*, **22**, ii, 439—442).—Ethyl formate

and succinate react in presence of potassium ethoxide free from potash, and the product, on suitable treatment, yields *ethyl formylsuccinate*, $C_9H_{11}O_5$; this may be purified by means of the solid compound which it forms with potassium carbonate, and which is decomposed by hydrochloric acid. The new substance is a colourless, limpid oil, which boils at $125-126^\circ$ under 16 mm. pressure; it has a pleasing, ethereal odour, and is miscible in all proportions with alcohol or ether, but is insoluble in water. It gives a deep violet coloration with ferric chloride, and, on treatment with hydroxylamine hydrochloride and alkalis, it yields an oil, probably consisting of the corresponding *oxime*.
W. J. P.

Ethyl Oxomalonate. By R. ANSCHÜTZ and E. PARLATO (*Ber.*, **25**, 3614—3617).—*Ethyl oxomalonate*, $CO(COOEt)_2$, is obtained by suspending dry barium mesoxalate in absolute alcohol and saturating the mixture with dry hydrogen chloride. It is a bright, greenish-yellow oil, of not unpleasant odour, boils at $100-101^\circ$ under 14 mm. pressure, and has a sp. gr. = 1.1358 at $16^\circ/16^\circ$. When treated with water, it is very easily converted into ethyl dihydroxymalonate, which melts at 57° .

Ethyl dihydroxymalonate cannot be distilled without decomposition; when heated under diminished pressure, it loses water at 40° , and is converted into ethyl oxomalonate; the water formed must, however, be carefully absorbed by phosphoric anhydride, otherwise ethyl dihydroxymalonate is reproduced.

Ethyl oxomalonate is also obtained by treating ethyl acetotartrate with the equivalent quantity of bromine, and distilling the product under diminished pressure.
E. C. R.

Isomerism of Fumaric and Maleïc acids. By S. TANATAR (*Annalen*, **273**, 31—55).—Most of the experiments here described have been previously published (Abstr., 1890, 1238; 1891, 174, 175; 1892, 1304, *et seq.*).

When silver malonate is warmed with a 30 per cent. solution of dibromacetic acid, carbonic anhydride is evolved, and silver bromide is deposited; the solution then contains a small quantity of fumaric acid, a little maleïc acid, a crystalline acid of the composition $C_4H_6O_5$, and a liquid acid. The crystalline acid, $C_4H_6O_5$, melts at $70-80^\circ$, is hygroscopic, and optically inactive; it does not give fumaric acid when heated with water at 200° , or when boiled with hydrochloric acid, but when distilled under reduced pressure, it yields fumaric acid and a larger proportion of maleïc acid; its salts are amorphous. The liquid acid yields fumaric acid and larger quantities of maleïc acid on distillation under reduced pressure, and on prolonged boiling with hydrochloric acid it gives a little fumaric acid; it is inactive, and its salts are amorphous.

If levulinic acid has the constitution $CH_2 < \begin{smallmatrix} CH_2 \\ COO \end{smallmatrix} > CMe \cdot OH$, as supposed by Anschütz, it is possible that it would have an abnormal heat of neutralisation; experiments showed that this was not the case.
F. S. K.

Homologues of Citraconic, Itaconic, and Mesaconic acids.

By V. SEMENOFF (*J. Russ. Chem. Soc.*, **23**, 430—443).—Ethyl-ethyl-acetoacetate was treated with bromine (2 mols.) either without a solvent, in ethereal solution, or under water. The product, after removal of the excess of bromine (and of the ether in the second case), was treated with excess of alcoholic potash, distilled with steam, acidified, and again distilled with steam. The residual solution, after being filtered to remove tarry matter, was evaporated to a smaller bulk, when small, brownish crystals separated on cooling. The mother liquor was extracted with ether, and from the ethereal extract a further quantity of organic acid was obtained, which was added to the first crop of crystals. The total yield of crude acid was about 25—30 per cent.; this was dissolved in dilute nitric acid, and boiled until the brown colour disappeared. On cooling and recrystallisation from water, the acid was obtained in colourless crystals.

Methylmesaconic acid, $C_6H_8O_4$.—The acid thus prepared is sparingly soluble in cold water, but easily in hot water or in ether. When crystallised from a boiling aqueous solution, it resembles fumaric acid in external appearance. It sublimes in needles which melt at 195—196°, and the alkali salts are easily soluble both in hot and in cold water. The calcium salt, $CaC_6H_6O_4 + 3\frac{1}{2}H_2O$, crystallises sometimes in stellate clusters of prisms, sometimes in single crystals. At 160° it becomes yellow, but does not part with all its water below 180°. The barium salt, $BaC_6H_6O_4 + 1\frac{1}{2}H_2O$, is precipitated in a finely crystalline state from its aqueous solution on adding alcohol; from a cold solution it separates in nodules. On reduction with sodium amalgam, the acid yields ethylsuccinic acid melting at 99—99.5°.

Methylcitraconic acid, $C_6H_8O_4$.—19 grams of methylmesaconic acid was heated for 10 hours in a sealed tube at 105—110° with 42 grams of acetic chloride. From the product an anhydride was obtained distilling at 142° under 66 mm. pressure; this combined only slowly with cold water, but rapidly with hot water, giving a solution from which methylcitraconic acid crystallised in the form of large, transparent prisms. This acid is very soluble in water or ether, easily in boiling chloroform, slightly in benzene, and insoluble in light petroleum. It melts at 95—96°, and decomposes at a comparatively low temperature into anhydride and water. An aqueous solution of the free acid yields the anhydride as a heavy, yellow oil on evaporation. The calcium salt, $CaC_6H_6O_4 + H_2O$, is more soluble in cold than in boiling water; so, likewise, is the barium salt, which crystallises with $1\frac{1}{2}$ mol. H_2O in hot solution, and with 4 mols. H_2O from a cold solution. The silver salt may be obtained as a fine, crystalline powder by precipitation.

A concentrated solution of methylcitraconic acid, heated for 10 hours at 140—150°, deposits *methylitaconic acid*, $C_6H_8O_4$, on cooling; this is crystalline, melts at 165—166°, is more soluble in water than methylmesaconic, but less soluble than methylcitraconic acid, and crystallises from a cold solution in clusters of prisms or tables. The transformation of methylcitraconic acid into its isomeride may be effected in the absence of water by heating for 24 hours at 100°. The calcium salt, $CaC_6H_6O_4 + H_2O$, separates as small scales when its

cold aqueous solution is heated to boiling; and the silver salt crystallises from its boiling solution in rhombohedra.

When ethylic propylacetoacetate is brominated and the product treated with alcoholic potash, *ethylmesaconic acid*, $C_7H_{10}O_4$, is obtained; this crystallises in small, colourless scales, little soluble in cold water, but easily soluble in boiling water and in ether. When gently heated, it sublimes in small needles melting at $172.5-173^\circ$. The calcium and barium salts are more soluble in cold than in hot water, and the silver salt becomes red on exposure to light. On reducing with sodium amalgam, the acid yields propylsuccinic acid.

Ethylcitraconic acid, $C_7H_{10}O_4$, is formed from ethylmesaconic acid similarly to the methyl compound. The anhydride boils at 152° under a pressure of 68 mm., and the acid melts at $92-94^\circ$, and crystallises from water in the form of large, transparent prisms. The calcium and barium salts, which crystallise with 1 mol. H_2O and $\frac{1}{2}$ mol. H_2O respectively, separate from their concentrated, cold aqueous solutions on boiling. The silver salt is an insoluble, crystalline powder.

Ethylcitraconic acid in aqueous solution is transformed into *ethylitaconic acid*, $C_7H_{10}O_4$, at 150° ; this is less soluble in water than either of its isomerides, and melts at $164-165^\circ$ after softening. The calcium salt, $CaC_7H_8O_4 + H_2O$, separates from the boiling solution in flocks; the silver salt, which is also flocculent, is soluble in water and blackens on boiling. Ethylitaconic acid, unlike its isomerides, is only reduced by sodium amalgam with great difficulty. J. W.

Stereochemical Notation: a Reply to Colson. By C. FRIEDEL (*Compt. rend.*, 115, 994—995).—The author points out that Colson (this vol., ii, 105, 106) has misrepresented Van't Hoff's schematic formulæ for the two active tartaric acids, probably through incorrectly translating the abridged notation. The author considers that the symbolic tetrahedron is much less likely to lead to confusion than any other method of representing optically active compounds.

C. H. B.

Constitution of Leucine. By E. SCHULZE (*Ber.*, 26, 56—57).—The author, in conjunction with Likiernik (*Abstr.*, 1891, 681), has shown that the inactive leucine obtained by them from conglutin is converted by nitrous acid into a hydroxy-acid which is identical with the acid obtained in a similar manner from the synthetical α -amidoisobutylacetic acid. It should also be identical with the leucic acid of Erlenmeyer and Sigl (*Ber.*, 7, 1109), but the authors found for their acid the melting point 52° , instead of $54-56^\circ$, as given by Erlenmeyer. After more careful purification, the author has now obtained his hydroxycaproic acid in crystals melting at 54.5° .

The action of *Penicillium glaucum* on the synthetical α -amidoisobutylacetic acid has again been investigated, the results agreeing with those previously obtained. The α -amido-acid obtained from fermentation caproic acid has also been subjected to the action of the same organism, but was found to give a solution of higher lævotatory power than the synthetical acid, which must therefore be different from the leucine obtained by the author. H. G. C.

Preparation of Zinc Ethide. By M. FILETI and A. CANTALUPO (*Gazzetta*, 22, ii, 387—388).—The authors prepare zinc ethide by exposing a mixture of zinc turnings, ethyl iodide, and a little zinc ethide to diffused light in an atmosphere of carbonic anhydride; after a week's time, all the ethyl iodide disappears, and on distilling the product in an atmosphere of carbonic anhydride, almost the theoretical yield of zinc ethide is obtained. W. J. P.

Derivatives of Nononaphthene. By M. KONOVALOFF (*J. Russ. Chem. Soc.*, 23, 446—451).—In the preparation of the monochloro-derivative of nononaphthene (b. p. 135—137°) there is formed a considerable quantity of a substance heavier than water and volatile with steam. This substance the author fractionated, first under reduced pressure, and then at atmospheric pressure in a current of carbonic anhydride; in this way, he succeeded in isolating a fraction boiling between 230° and 235°, which had the composition $C_9H_{16}Cl_2$. This dichloride has the sp. gr. 1.1035 at 0°/0°, and does not solidify in a mixture of ice and salt. Aniline abstracts hydrogen chloride from the molecule only at a very high temperature, and even then incompletely. By heating, however, with dry sodium acetate (2 mols.) and glacial acetic acid (2 mols.) for five hours at 200°, a considerable quantity of unsaturated hydrocarbon was obtained, which was dried and fractionated over sodium; all the fractions were colourless, but rapidly became brown on exposure to air. The lower fractions were volatile with steam, and boiled chiefly between 139° and 152°. The portion boiling at 139—141° gave numbers, on analysis, closely approximating to those required by the formula C_9H_{14} . This hydrocarbon, in acetic acid solution, is at once attacked by bromine at a low temperature, with formation of a crystalline powder easily soluble in alcohol and ethyl acetate, soluble with difficulty in ether, and almost insoluble in boiling benzene. The crystals from a weak acetic acid solution form long, silky needles. The bromide rapidly decomposes in the air, a tarry mass being formed; and the dry substance is carbonised at 70°.

The fraction boiling at 305—315° has also the formula C_9H_{14} , but freezing point determinations in benzene give a molecular weight nearly corresponding with the formula $(C_9H_{14})_2$. It is a heavy oil, and forms a tarry mass both with bromine and with dry hydrogen chloride. J. W.

Action of Nitric and Nitrous acids on certain Organic Substances. By A. ANGELI (*Gazzetta*, 22, ii, 325—340; compare Abstr., 1892, 447 and 1198).—Cramer's demonstration (Abstr., 1892, 699) that the substance obtained by Pröpper by the action of nitric acid on ethyl acetoacetate contains the group $\begin{array}{c} -C:N\cdot O \\ | \\ -C:N\cdot O \end{array}$, gives weight to the author's opinion that eulyte (*Gazzetta*, 21, ii, 32) contains this group. The author was unable to obtain an analogous compound by the action of nitric acid on bromocitraconic acid.

The action of nitric acid on phenacylacetone would be expected to

yield a substance similar to eulyte, as does acetonylacetone (Abstr., 1891, 890); this, however, is not the case, a *substance* of the composition $C_{22}H_{18}N_4O_{11}$ being formed. This crystallises in white scales, melts at 210° , and is insoluble in alkalis and alkaline carbonates.

Ethyl isodehydracetate reacts readily with fuming nitric acid, yielding a *nitro*-derivative (?) of the composition $C_9H_9NO_5$, which separates from benzene in magnificent, yellowish crystals melting at 98° . It is insoluble in alkali carbonates, but dissolves slowly in alkalis.

The action of nitrous acid on a large number of substances is discussed, and several of the products obtained by its action on aromatic compounds are described.

Isosafrole yields a *nitrosite*, $CH_2 \cdot O_2 \cdot C_6H_3 \cdot C_3H_5N_2O_3$, with nitrous acid; it forms white, microscopic crystals melting with decomposition at about 130° . It is almost insoluble in most solvents, and its *anhydride*, $CH_2 \cdot O_2 \cdot C_6H_3 \cdot C_3H_3N_2O_2$, forms yellow needles melting at 124° without decomposition; this is very soluble in benzene, but only sparingly in alcohol. It dissolves in sulphuric acid, and is precipitated unchanged with water.

Methyleugenol nitrosite anhydride, $C_6H_3(OMe)_2 \cdot C_3H_3N_2O_3$, forms yellow needles melting at 118° , and closely resembles the preceding compound.

Isopiole nitrosite, $CH_2 \cdot O_2 \cdot C_6H(OMe)_2 \cdot C_3H_3N_2O_3$, melts at about 132° , whilst its *anhydride* forms yellow needles melting at 170° .

Isobutenylphenyl nitrosite, $C_6H_5 \cdot C_4H_7N_2O_3$, forms beautiful, colourless needles melting at 112° with decomposition.

The author concludes that the action of nitrous acid on unsaturated aromatic substances affords a means of ascertaining whether a double bond in the side chain is contiguous to the aromatic nucleus or not; with such substances a nitrosite cannot be prepared, whilst if the unsaturated side chain be united to the nucleus by a single bond, a nitrosite will be formed on treatment with nitrous acid.

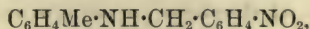
W. J. P.

Action of Hydrogen Peroxide on Aniline. By E. SCHUNCK and L. MARCHLEWSKI (*Ber.*, 25, 3574–3577).—The lake obtained by Leeds by the action of hydrogen peroxide on aniline was regarded by Schunck and Brebner as dianilidobenzoquinoneanilide. In confirmation of this view, the authors now find that when aniline is heated on the water-bath with a solution of hydrogen peroxide in dilute acetic acid, ammonia, azobenzene, and dianilidoquinoneanilide are the products. When, however, a solution of hydrogen peroxide in dilute hydrochloric acid is employed, a compound is formed which perhaps is an induline. In view of the possibility that azobenzene is the primary product of the action, and to throw light on the formation of the anilidoquinone, the authors examined the reaction between azobenzene and a boiling acid solution of hydrogen peroxide, without, however, recognising with certainty the production of quinone. It may, therefore, be assumed that the azobenzene, at the moment of its formation, reacts with the hydrogen peroxide, giving rise to quinone, which then acts on the excess of aniline.

A. R. L.

Paraxylinine. By R. MICHAEL (*Ber.*, 26, 39).—When pure paraxylinine is exposed to a very low temperature for a long time, it crystallises in large, colourless plates, frequently united in twins. It melts at 15.5°, and boils at 213.5° (uncorr.) under 762 mm. pressure. The *acetyl* compound melts at 139.5°. H. G. C.

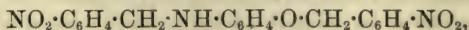
Some Nitro- and Amido-benzylated Bases. By E. LELLMANN and N. MAYER (*Ber.*, 25, 3581—3586).—*Orthodinitrodibenzylparatoluidine*, $C_6H_4Me \cdot N(CH_2 \cdot C_6H_4 \cdot NO_2)_2$, is prepared by boiling an alcoholic solution of orthonitrobenzyl chloride (2 mols.) and paratoluidine for half an hour, evaporating the alcohol, and heating the residue with aqueous sodium carbonate for some hours at 110—120°; it crystallises in yellow needles, melts at 160°, and is sparingly soluble in alcohol and ether. *Paradinitrodibenzylparatoluidine* forms yellow crystals, and melts at 189°. Only one nitrobenzyl residue can be introduced into orthotoluidine. *Orthonitrobenzylorthotoluidine*,



melts at 96°; *paranitrobenzylorthotoluidine* crystallises in bright red needles, and melts at 93°; whilst *paranitrobenzylparatoluidine* forms yellow crystals, and melts at 68°.

Orthodinitrodibenzylmetadiamidobenzene, $C_6H_4(NH \cdot CH_2 \cdot C_6H_4 \cdot NO_2)_2$, is prepared by heating an alcoholic solution of 1:2-diamidobenzene hydrochloride (1 mol.) and orthonitrobenzyl chloride (2 mols.) on the water-bath; it separates in green crystals, and melts at 134°. *Orthodinitrodibenzylorthodiamidotoluene* forms red crystals, and melts at 129°.

Orthonitrobenzylmetamidophenyl orthonitrobenzyl ether,



is obtained by heating metamidophenol (1 mol.) with orthonitrobenzyl chloride (2 mols.) and sodium acetate (2 mols.) in alcoholic solution; it forms dark brown crystals, melts at 190°, and is insoluble in alkalis.

Orthonitrobenzyl orthonitrophenol ether, $NO_2 \cdot C_6H_4 \cdot OCH_2 \cdot C_6H_4 \cdot NO_2$, is formed by heating equivalent quantities of potassium orthonitrophenol and orthonitrobenzyl chloride, dissolved in alcohol, on the water-bath; it crystallises in colourless needles, and melts at 154°. None of the new dinitro-derivatives described above could be converted into azo-compounds by treating them with alkaline stannous chloride.

Orthodiamidodibenzylaniline, $NPh(CH_2 \cdot C_6H_4 \cdot NH_2)_2$, is obtained by cautiously reducing the corresponding dinitro-base with stannous chloride and hydrochloric acid at 0°, and treating the resulting *stannochloride* with ammonium sulphide; it forms colourless crystals, and melts at 187°. *Orthodiamidodibenzylparatoluidine* crystallises in small, colourless needles, and melts at 145°; the *hydrochloride* crystallises with 3 mols. H_2O , and the *sulphate* with 4 mols. H_2O . A. R. L.

Propylamidophenol and its Acetyl Derivatives. By P. CAZENUEVE (*Compt. rend.*, 115, 1312—1315).—When the propylamidophenol obtained from camphor (this vol., i, 152) is simply mixed with excess of acetic anhydride, there is a distinct and immediate rise of temperature, and if the product is precipitated with water and recrystallised from alcohol of 93°, the compound $\text{OH}\cdot\text{C}_9\text{H}_{10}\cdot\text{NHAc}$ is obtained in colourless prisms, which melt at 95—96° and are insoluble in water, but very soluble in chloroform, alcohol, and ether. It is insoluble in all acids, but dissolves in alkalis; an alcoholic solution gives an apple-green coloration with ferric chloride.

If the propylamidophenol is boiled with excess of acetic anhydride for 15 minutes, even without any sodium acetate, the *triacetyl* derivative, $\text{OAc}\cdot\text{C}_9\text{H}_{10}\cdot\text{NAc}_2$, is obtained, and, when recrystallised from alcohol, forms white, very light, slender needles. It melts at 138—139° to a colourless liquid, which readily remains in superfusion; at 200—250° under ordinary pressure, it distils with slight decomposition and liberation of acetic acid. It is insoluble in water, ether, benzene, and carbon bisulphide, and also in acids and alkalis, but dissolves readily in alcohol or chloroform. When boiled with water containing hydrochloric or sulphuric acid, it remains unaltered, but when boiled with a solution of an alkali hydroxide, it dissolves with hydrolysis, and afterwards undergoes further decomposition, the liquid becoming first yellow and then red.

Propylamidophenol in alkaline solution is an energetic developer of photographic plates, and hence, if Lumière's laws are correct (*Bull. Soc. Chim.*, 1892), the hydroxyl and amido-groups must be in the ortho- or para-position, and not in the meta-position, as assumed in a previous paper (*loc. cit.*). The para-position is improbable, but the ortho-position agrees well with the properties of the compound. Further researches have shown also that the compound from which the propylamidophenol is formed is a nitrophenol, and not a nitroketone as originally supposed.

C. H. B.

Alkyl Orthodiamines. By F. KEHRMANN and J. MESSINGER (*J. pr. Chem.* [2], 46, 565—574; compare *Abstr.*, 1892, 1472).—Ortho-nitrobenzylaniline melts at 74—75°, and orthonitromethylaniline at 34°.

New bases have been obtained by the oxidation of methyl- and ethyl-orthophenylenediamine by ferric chloride; the analysis of the hydrochloride of the methyl derivative corresponds with the formula $\text{C}_{14}\text{H}_{16}\text{N}_3\text{OCl} + \text{H}_2\text{O}$. Treatment of orthamidodiphenylamine with ferric chloride, yields a base, $\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}$, which crystallises in brownish-red laminæ, having a bluish lustre, melts at 189—190°, and is soluble in most solvents, except water and cold alcohol. The constitution of these bases is not settled, but the probabilities are here discussed.

Dinitrophenylphenylorthophenylenediamine



prepared from dinitrobenzene and orthamidodiphenylamine heated together with sodium acetate, forms red, prismatic crystals,

melts at 170—171°, and is nearly insoluble in water, alcohol, and ether.

Paracetamidorthonitrodiphenylamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{COMe}$, from paramidoacetanilide, sodium acetate, and orthonitrobromobenzene, crystallises in reddish-yellow laminæ, and melts at 147—148°.

Paranitrorthamidomethylaniline [$\text{NHMe} : \text{NH}_2 : \text{NO}_2 = 1 : 2 : 4$], obtained by reducing orthoparadinitromethylaniline, crystallises in dark red prisms, and melts at 177—178°. When a dilute hydrochloric acid solution of the base is mixed with pyrotartaric acid, a yellow, crystalline precipitate of methylketomethylnitrodihydroquinoxaline, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \begin{smallmatrix} \text{N} = \text{CMe} \\ | \\ \text{NMe} \cdot \text{CO} \end{smallmatrix}$, is obtained; it has an intensely bitter taste.

A. G. B.

Dibenzoyldiamidoethylene. By E. BAMBERGER and B. BERLÉ (*Ber.*, **25**, 3653—3654).—The authors have previously shown (*Abstr.*, 1892, 632) that dibenzoyldiamidoethylene is formed by the action of benzoic chloride and soda on glyoxaline; on treating the amido-derivative with glacial acetic acid, it is converted into a second compound, having the same percentage composition and molecular weight as the dibenzoyldiamidoethylene, but differing from it in many of its chemical and physical properties; neither of these compounds is acted on by alcoholic potash, and their relationship is probably similar to that of maleïc and fumaric acids.

J. B. T.

Diazobenzene. By A. WOHL (*Ber.*, **25**, 3631—3634).—A *benzoyl derivative* of diazobenzene, of the formula $\text{NO} \cdot \text{NPh} \cdot \text{COPh}$, is obtained on agitating a freshly prepared solution of potassium diazobenzene with excess of benzoic chloride. It crystallises in pale yellow needles, melts at 67° with explosive decomposition, and decomposes with evolution of gas when warmed in solution. It yields benzanilide when exposed to the air for 2—3 days, or when reduced with zinc-dust and acetic acid or ammonium sulphide. When treated with phenylhydrazine, it is converted into benzanilide and nitrous acid.

Silver diazobenzene, PhN_2OAg , is obtained by adding silver nitrate to a dilute alkaline solution of diazobenzene. It is a greyish-white powder, explodes very easily when dry, even when rubbed with a spatula, and decomposes in a capillary tube at 118°. When warmed with dilute nitric acid, it dissolves with a deep yellow coloration and the odour of nitrophenol. When heated with water above 65°, it is decomposed. This salt, therefore, differs from the stable silver diazobenzene prepared by Griess (*Annalen*, **137**, 54).

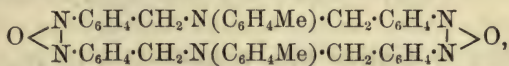
The alkaline solution of the silver salt, when treated with excess of ethyl iodide, yields a yellow oil containing nitrogen; it is not explosive, and is easily volatile with steam.

E. C. R.

Azo- and Hydrazo-benzyl Alcohols. By C. NEUBERT (*J. pr. Chem.* [2], **46**, 580—581).—A compound, $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2$, is obtained by heating orthohydrazobenzoic acid (m. p. 205°) with acetic anhydride (in mol. prop.) and subliming the product; it crystallises in greenish-

yellow needles, and melts at 293° . The following have been prepared and will shortly be further described:—*Orthazobenzyl alcohol*, $\text{N}_2(\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH})_2$, red laminæ, m. p. 165° . *Orthohydrazobenzyl alcohol*, $\text{N}_2\text{H}_2(\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH})_2$, yellow laminæ, m. p. $123\text{--}124^{\circ}$. *Parahydrazobenzyl alcohol*, white flocculi, m. p. 196° . *Parazobenzyl alcohol*, dark red needles, m. p. above 300° .
A. G. B.

Intramolecular Formation of the Azo-group. By E. LELL-MANN and N. MAYER (*Ber.*, **25**, 3578—3580; compare Abstr., 1892, 890).—*Orthazodibenzylaniline*, $\text{NPh} < \begin{smallmatrix} \text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N} \\ \text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N} \end{smallmatrix}$, is obtained by heating on the water bath a saturated solution of orthodinitrodibenzylaniline in toluene with an excess of an alkaline solution of stannous chloride and an equal volume of alcohol; it crystallises in red needles, melts at 226° , and is sparingly soluble in cold benzene. *Orthazodibenzylparatoluidine*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N} < \begin{smallmatrix} \text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N} \\ \text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N} \end{smallmatrix}$, is prepared in a manner similar to the aniline compound, which it resembles, and melts at 211° . When but a slight excess of stannous chloride is used in the last experiment, a red, amorphous *azoxy*-derivative,



may also be isolated. Experiments which are now in progress show that nitro-compounds of the type $\text{RN}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, where R is an alkyl-group, give rise to the corresponding amido-derivatives on reduction in alkaline solution.
A. R. L.

Diazoamido-compounds. By S. NIEMENTOWSKI (*Ber.*, **26**, 49—55).—It is usually supposed that the action of 1 mol. of nitrous acid on 1 mol. of an amido-compound always brings about the formation of the diazo-compound alone, but the author has observed cases in which a large quantity of the diazoamido-compound is formed under these conditions. So far as his experiments have gone at present, it appears that amido-compounds having neutral or only slightly acid properties yield considerable quantities of diazoamido-derivatives, whilst the strongly basic amido-compounds and those containing an acid group such as carboxyl yield solely the diazo-compounds. In the present paper, the results obtained in the treatment of orthamidoparatolunitrile are discussed.

The preparation of diazoamidoparatolunitrile has been described in a previous paper (*Monatsh.*, **10**, 591); the author has now investigated the yield given under different conditions, and finds that when 1 mol. of nitrous acid is used for 2 mols. of the amido-compound, a quantitative yield of the diazoamido-derivative is obtained as usual; moreover, if they are mixed in molecular proportion, the yield still amounts to 60 per cent., but it is decreased by the addition of excess of acid, until with a very large proportion of the latter the diazo-derivative is the sole product. Diazoamidotolunitrile is converted by boiling alkali into metahomanthranilic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{COOH}$,

and resinous products, probably formed from the metahomosalicylic acid, which is one of the primary products of the hydrolysis.

The metahomanthranilic acid, when diazotised under the conditions which give a yield of 60 per cent. of the diazoamido-derivative with amidotoluonitrile, forms solely the diazo-compound, probably owing to the presence of the strongly acid carboxyl-group.

Diazoamidoparatoluonitrile is acted on by α - and β -naphthol and by resorcinol with formation of azo-derivatives of paratoluonitrile, a more or less complete hydrolysis taking place simultaneously, so that azo-compounds of the corresponding metahomanthranilic acid are also obtained. These may also be directly obtained by the action of the phenols on the diazo-compound of the acid. β -Naphtholazoparatoluonitrile, $\text{CN}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, forms long, blood-red, lustrous needles, melts at 272° , and dissolves in concentrated sulphuric acid with a cherry-red colour. The corresponding β -naphtholazoparatoluic acid, $\text{COOH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, crystallises in long, pale-red needles, and melts at 283° ; α -naphtholazoparatoluic acid crystallises from acetic acid in slender matted needles, and melts at 270° with decomposition. Resorcinol yields with diazoamidoparatoluonitrile chiefly resorcinol-disazoparatoluonitrile, $\text{C}_6\text{H}_2(\text{OH})_2(\text{N}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CN})_2$, which is a brick-red, amorphous compound, and melts with decomposition at 287° .

H. G. C.

Conversion of Amines into Diazoimides by means of Azoimide. By E. NOELTING and O. MICHEL (*Ber.*, 26, 86—87).—Diazoimides are formed on adding a solution of sodium nitride or hydrogen nitride to a solution of a diazo-compound containing an excess of sulphuric acid. In this way, the authors have prepared diazoimides from aniline, ortho-, meta-, and para-nitranilines, 1, 2, 4-dinitraniline, and sulphanilic acid.

1, 2, 4-Dinitrodiazobenzeneimide, as obtained by this method, crystallises from dilute alcohol in white needles, and melts at 65° with decomposition.

E. C. R.

Action of Diazo-compounds on Hydrazines. By E. NOELTING and O. MICHEL (*Ber.*, 26, 88—92).—According to Fischer (*Ber.*, 10, 1334), diazobenzeneimide and aniline are formed by mixing a solution of a phenylhydrazine salt with one of a diazobenzene salt. Griess (*Ber.*, 9, 1659) obtained diazobenzeneimide, diazobenzeneimidecarboxylic acid, aniline, and amidobenzoic acid both by the action of diazometamidobenzoic acid on phenylhydrazine, and also by the action of diazobenzene on metahydrazinebenzoic acid. He also found that by the action of diazosulphanilic acid and diazonaphthionic acid on phenylhydrazine and of diazobenzene on parahydrazinebenzenesulphonic acid, both the diazo-compound and the hydrazine are converted into azoimides (*Ber.*, 20, 1528).

When a solution of diazobenzene sulphate containing sufficient sodium acetate to neutralise the free mineral acid is added to an ice-cold solution of hydrazine sulphate, diazobenzeneimide, and ammonium sulphate are formed together with a small quantity of a compound which crystallises from alcohol in white needles. Neither

aniline nor hydrogen nitride could be detected in the products of the reaction.

Ortho-, meta-, and para-nitrodiazobenzene sulphates and hydrazine in the same way give theoretical yields of the diazoimide and ammonium sulphate. In no case was nitraniline and hydrogen nitride detected in the product.

1:2:4-Dinitrodiazobenzene sulphate in the same way yields dinitrodiazobenzeneimide, in a crystalline condition, and ammonia.

Diazosulphanilic acid and hydrazine yield ammonia and diazobenzeneimidesulphonic acid. The latter is isolated by means of its phenylhydrazine salt.

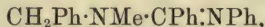
E. C. R.

Action of Phenylcarbimide on Benzylbenzaldoxime. By E. BECKMANN and E. FELLRATH (*Annalen*, **273**, 1—30).—Beckmann (Abstr., 1891, 193) has stated that the compound melting at 122°, prepared by Goldschmidt (Abstr., 1890, 1412; 1891, 1477) and by Beckmann (*loc. cit.*), by treating β -benzylbenzaldoxime with phenylcarbimide, is decomposed by sodium ethoxide, yielding carbonic anhydride and a phenylimido-base of the composition $C_{20}H_{18}N_2$, which melts at 100°. The objects of this work were to try and ascertain the constitution of this base, and to obtain further information with regard to the action of phenylcarbimide in general. Although the former of these objects has been accomplished, the mechanism of the reaction by which the phenylimido-base is formed from β -benzylbenzaldoxime still requires elucidation.

The phenylimido-base is produced, but only in very small quantities, when β -benzylbenzaldoxime is treated with phenylthiocarbimide.

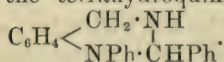
The phenylimido-base combines with methyl iodide at the ordinary temperature, yielding a substance which forms large, monoclinic crystals and which contains iodine; when this iodo-compound is treated with potash, it gives a base which crystallises in well-defined, monoclinic crystals, melts at 90·5°, and seems, from analyses and molecular weight determinations, to have the molecular formula $C_{21}H_{20}N_2$.

As it seemed probable, considering its origin and method of formation, that the base melting at 90·5° had the constitution

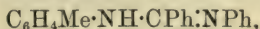


its synthesis from benzylmethylamine, $CH_2Ph \cdot NHMe$, and benzanilid-imidochloride, $CPhCl \cdot NPh$, was attempted. When these two substances are heated together at 100°, they combine to form a crystalline hydrochloride, which, on treatment with potash, gives a crystalline base of the molecular formula $C_{21}H_{20}N_2$; this base forms well-defined crystals, melts at 67°, and is evidently not identical with the base melting at 90·5°. Nevertheless, a phenylimido-base melting at 100°, and identical with the compound obtained from the product of the action of phenylcarbimide on β -benzylbenzaldoxime, can be directly prepared by treating benzanilidimidochloride with benzylamine; this fact shows that in the phenylimido-base the carbon and nitrogen atoms are combined in the order given in the amidine

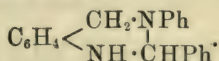
formula, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CPh}\cdot\text{NPh}$, but it does not exclude as impossible the tetrahydroquinazoline constitution represented by the formula



In order to settle the question of the constitution of the phenylimido-base, the products of the interaction of benzanilidimidochloride and other amido-compounds were studied. A base of the molecular formula $\text{C}_{20}\text{H}_{18}\text{N}_2$ is obtained when benzanilidimidochloride is treated with orthotoluidine, and the hydrochloride produced in this way decomposed with potash; it crystallises in small, colourless needles, and melts at 110° . If reduced with sodium amalgam in boiling alcoholic solution, it yields a mixture of bases, which, when shaken with potash and benzenesulphonic chloride, gives orthotoluidinephenylsulphone, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$ (m. p. 124°), and benzylanilinephenylsulphone, $\text{CH}_2\text{Ph}\cdot\text{NPh}\cdot\text{SO}_2\text{Ph}$. The last-named compound crystallises from alcohol in long needles, melts at 119° , and is easily separated from the other sulphone, as it is insoluble in potash. The readiness with which reduction takes place and the nature of the compounds so formed show that the original base, melting at 110° , is an *orthotolylphenylbenzenylamidine* of the constitution



and not a tetrahydroquinazoline of the constitution



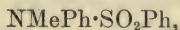
The base of the molecular formula $\text{C}_{26}\text{H}_{22}\text{N}_2$, prepared from benzanilidimidochloride and benzylaniline in like manner, melts at 111° ; on reduction with sodium amalgam, it yields benzylaniline, so that it is doubtless a *phenylbenzylphenylbenzenylamidine* of the constitution $\text{CH}_2\text{Ph}\cdot\text{NPh}\cdot\text{CPh}\cdot\text{NPh}$.

The results of the experiments just described having indicated a method by which the constitution of the phenylimido-base could be determined, the compound in question was reduced with sodium amalgam and the products separated with the aid of soda and benzenesulphonic chloride; in this way, *benzylaminephenylsulphone*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$, melting at 87° , *benzylanilinephenylsulphone*, melting at 119° , and small quantities of *anilinephenylsulphone*, melting at 109° , were obtained, so that the phenylimido-base is doubtless a *benzylphenylbenzenylamidine* of the constitution given above; this view is confirmed by the fact that, as a secondary base, it interacts with benzenesulphonic chloride, yielding a compound melting at 148° , and also with benzyl chloride, forming an oily benzyl derivative.

When the base melting at 67° , obtained by the action of benzylmethylamine on benzanilidimidochloride, is reduced with sodium amalgam, it is decomposed into aniline, benzylaniline, and benzylmethylamine, which can be separated with the aid of benzenesulphonic chloride; *benzylmethylaminephenylsulphone*, $\text{CH}_2\text{Ph}\cdot\text{NMe}\cdot\text{SO}_2\text{Ph}$, crystallises from a mixture of ether and light petroleum in well-defined plates melting at 93° . When the base melting at 67° is

heated with hydrochloric acid at about 200° , it is decomposed into aniline, benzylmethylamine, and benzoic acid. These reactions show that the base is a *benzylmethylphenylbenzenylamidine* of the constitution represented by the formula $\text{CH}_2\text{Ph}\cdot\text{NMe}\cdot\text{CPh}\cdot\text{NPh}$.

The base melting at $90\cdot5^{\circ}$, prepared by methylating the phenylimido-base, is reduced by sodium amalgam in alcoholic solution, yielding dibenzylamine and methylaniline, which can be separated with the aid of benzenesulphonic chloride; *dibenzylaminephenylsulphone*, $\text{SO}_2\text{Ph}\cdot\text{N}(\text{CH}_2\text{Ph})_2$, and *methylanilinephenylsulphone*,



are crystalline compounds melting at 68° and 79° respectively. The base melting at $90\cdot5^{\circ}$ is also decomposed by concentrated hydrochloric acid at 200° , yielding methylaniline, benzyaniline, and benzoic acid. When treated with bromine in chloroform solution, the base is converted into a colourless compound of the composition $\text{C}_{21}\text{H}_{20}\text{N}_2\text{Br}_2$, which melts at $228\text{--}229^{\circ}$ with decomposition; this bromo-derivative is readily decomposed by cold alcoholic silver nitrate, yielding a compound of the composition $\text{C}_{21}\text{H}_{19}\text{N}_2\text{Br}$, which crystallises in plates and melts at 102° . These reactions show that the base is a *phenylmethylbenzylbenzenylamidine* of the constitution represented by the formula $\text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{CPh}\cdot\text{NMePh}$.

Attempts to prepare the compound (benzylphenylcarbamide) melting at 168° , which, according to Goldschmidt (*Ber.*, **23**, 2746), is produced by the action of phenylcarbimide on β -benzylbenzaldoxime were unsuccessful.

F. S. K.

Action of Amines and Ammonia on the Dinitrosacyls. By A. F. HOLLEMAN (*Rec. trav. Chim.*, **11**, 258—274; compare Abstr.,

1889, 50; 1892, 971).—*Diphenyldinitrosacyl*, $\begin{matrix} \text{CBz}\cdot\text{N}\cdot\text{O} \\ | \\ \text{CBz}\cdot\text{N}\cdot\text{O} \end{matrix}$, is prepared

by treating acetophenone with red nitric acid for 24 hours at the ordinary temperature. The product is washed with water and recrystallised from ether and glacial acetic acid, and amounts to 75 per cent. of the acetophenone used. It forms colourless, monoclinic tablets, of which full crystallographic details are given:— $a:b:c = 1\cdot6156:1:1\cdot6021$; $\beta = 61^{\circ} 41'$. When diphenyldinitrosacyl is heated at 100° with dry aniline in ethereal solution, it is decomposed into benzanilide and a dark-brown, crystalline substance, which, on further cautious heating, is converted into a yellow, crystalline substance melting at 205° , and having the composition $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}_2$. This is much more stable than the dinitrosacyl, as it resists the action of concentrated hydrochloric acid at 110° ; on boiling with strong potash, however, it is decomposed into ammonia, aniline, and benzoic acid. It is probably formed by the condensation of a second aniline

molecule with the residue, $\begin{matrix} \text{CBz}\cdot\text{N}\cdot\text{O} \\ | \\ \text{CH}\cdot\text{N}\cdot\text{O} \end{matrix}$, left after the removal as benzanilide of one of the benzoyl groups of the dinitrosacyl, and has therefore, the constitution, $\begin{matrix} \text{CBz}\cdot\text{N}\cdot\text{NPh} \\ | \\ \text{CH}\cdot\text{N}\cdot\text{O} \end{matrix}$. By the further action of

aniline the second benzoyl group is also detached as benzanilide, whilst at the same time diphenylcarbamide is formed. The latter also results directly by boiling an aniline solution of the dinitrosacyl for some time. This formation of diphenylcarbamide bears a certain analogy to that of phenylcarbamide and diphenylguanidine by the action of aniline on mercuric fulminate, and suggests that the nucleus $C_2N_2O_2$ is the same in both fulminate and dinitrosacyl (compare Abstr., 1892, 64, 446), a view which is confirmed by the formation of a small quantity of guanidine along with benzamide, when diphenyldinitrosacyl is heated with 20 per cent. aqueous ammonia for three hours at $120-140^\circ$.

When paratoluidine is substituted for the aniline, the action is analogous, the product forming brilliant needles, melting at 210° , and having the composition $C_{16}H_{13}N_3O_2$. With alcoholic ammonia at 100° , a red product is formed, which on purification yields a substance crystallising in long, brilliant, white needles, melting at 135° , and having the composition $C_9H_7N_3O_2$. It is completely broken up by prolonged heating with aqueous ammonia.

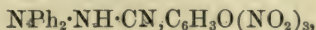
Dianisylidinitrosacyl behaves in a similar way with aniline, anis-anilide and a white, crystalline substance melting at 125° , and having the composition $C_{16}H_{13}N_3O_3$, being formed.

Methylaniline has no action on the dinitrosacyls.

JN. W.

Phenylanilcyanamide and β -Diphenylsemithiocarbazide.

By D. TIVOLI (*Gazzetta*, 22, ii, 379—386; compare Abstr., 1892, 1323).—On passing cyanogen chloride into an ethereal solution of diphenylhydrazine, the hydrochloride of the base separates and *phenylanilcyanamide*, $NPh_2 \cdot NH \cdot CN$, remains in solution; this forms colourless crystals melting at 97° , and when pure is unaltered on exposure to the air. It is very soluble in alcohol or benzene, less so in acetic acid, and insoluble in water; it is decomposed by acids, and, with dilute potash, gives an intense blue liquid. It gives the normal molecular weight by the cryoscopic method in acetic acid solution. The *hydrochloride*, $NPh_2 \cdot NH \cdot CN, 2HCl$, forms minute, white needles melting at 162° ; it is very soluble in alcohol, sparingly so in light petroleum, chloroform, or benzene, and insoluble in ether. It does not reduce Fehling's solution, but reduces ammoniacal silver nitrate, and with dilute copper sulphate solution, gives a magnificent red coloration, soon changing to violet. It reduces platonic and auric chlorides without combining with the salts. Its aqueous solution soon decomposes with separation of the base, which is best prepared in the pure state by this means. The *picrate*,

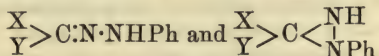


is obtained in large, garnet-coloured crystals, which melt at 172° with decomposition; it is very soluble in benzene, and sparingly so in alcohol, ether, and water. On rapid heating, it decomposes explosively with carbonisation.

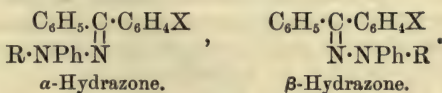
β -Diphenylsemithiocarbazide, $NH_2 \cdot CS \cdot NH \cdot NPh_2$, is obtained by the action of ammonium sulphide on phenylanilcyanamide in alcoholic solution. It forms beautiful, colourless crystals, melts at 202° , and

gives a normal molecular weight by the cryoscopic method in acetic acid solution. It has a bitter taste, is very soluble in alcohol, benzene, chloroform, acetic acid, or acetone, sparingly so in ether, and insoluble in water or light petroleum. W. J. P.

Stereochemistry of Unsymmetrical Hydrazones. By A. HANTZSCH (*Ber.*, **26**, 9—17; compare Abstr., 1892, 338, 798, and following abstract).—The existence of stereochemically isomeric hydrazones of unsymmetrical ketones, $X \cdot CO \cdot Y$, has been proved in the case of the phenylhydrazone of anisyl phenyl ketone, and the diphenylhydrazones (unsymmetrical) of anisyl phenyl and paratolyl phenyl ketones. In these and other cases, only one, the α -, hydrazone is obtained by the action of the hydrazine on the ketone itself, but if, instead of the ketone, its chloride, $X \cdot CCl_2 \cdot Y$, be used, then, in each of the cases above mentioned, two isomeric crystalline hydrazones are obtained. (In other cases an oil was obtained which could not be induced to crystallise, and was probably a mixture of the two isomerides.) The two substances are structurally identical, for they have the same composition, the same molecular weight as determined by Raoult's method, and are both decomposed by alcoholic hydrochloric acid into ketone and hydrazine. That they are isomeric, however, is evident from their difference in melting point, solubility, and chemical behaviour. But the isomerism is geometrical and not structural, for were it the latter, then a symmetrical ketone, $X \cdot CO \cdot X$, such as benzophenone, ought equally to yield two hydrazones, but this is not the case; further, the two possible structurally isomeric formulæ



represent the isomerism as conditioned by the presence of a "mobile hydrogen atom." But it cannot be thus conditioned, for the diphenylhydrazones also exhibit isomerism of this kind, although in them the "mobile hydrogen atom" is absent, being replaced by phenyl. It is therefore necessary to have recourse to geometrical formulæ for an explanation. The following formulæ are proposed, and, in assigning the second to the less stable β -hydrazone, the analogy with the isomeric oximes was used as a guide; in the case of these compounds, it is the less stable configuration which has the OH of the oximido-group nearer to the substituted phenyl.

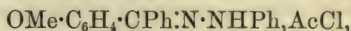


The α -isomerides are more stable, more soluble, and have a higher melting point, than the β -compounds. The latter are almost entirely converted into the former by the action of hydrogen chloride, and by the successive action of acetic chloride and ammonia; by the latter method, however, a conversion of the α - into the β -variety can also be effected, but only to a very slight extent.

The paper also contains an attempted refutation of Auwers and V. Meyer's stereochemical formulæ for isomeric hydrazones, and, as an appendix, a reply by Meyer to these objections. C. F. B.

Stereochemical Phenylhydrazones and Diphenylhydrazones. By B. OVERTON (*Ber.*, **26**, 18—34).—This paper contains the experimental matter on which the deductions in the preceding abstract are based. The stereochemically isomeric hydrazones were obtained by mixing the ketochloride with the hydrazine in ethereal, or sometimes in acetic acid solution, great care being taken that all the materials were quite pure. When the reaction was complete, often only after several days, the phenylhydrazine chloride was filtered off, any excess of phenylhydrazine removed by shaking with hydrochloric acid, and the ethereal solution allowed to evaporate at the ordinary temperature. The α -hydrazone crystallises first, and then the β -; the yield of the latter was never greater than about 10 per cent. By the action of the hydrazine on the ketone, the α -variety only was obtained.

Anisyl phenyl ketochloride yields, with phenylhydrazine, an α -hydrazone, forming colourless, ill-defined crystals melting at 132° , and a β -hydrazone, which forms a pale-coloured powder, or small, transparent, crystalline scales, and melts at 90° ; both of these dissolve in acetic chloride, yielding an additive compound,



which forms a transparent, horny mass, decomposed by water into ketone and acetylphenylhydrazine, by ammonia into the hydrazone and acetamide. With benzoic chloride, an analogous reaction occurs. With diphenylhydrazine, the ketochloride yields an α -diphenylhydrazone crystallising in yellow prisms, and melting at 151 — 152° , and a somewhat darker β -compound melting at 115° . These are much more stable than the monophenyl compounds, and no cases of inter-conversion were observed.

Paratolyl phenyl ketone yields, with phenylhydrazine, the α -hydrazone in fine, white crystals melting at 109° . If the ketochloride is used, an oily product is obtained, from which no crystalline substance could be separated. With diphenylhydrazine, two diphenylhydrazones were obtained: the α - in yellow crystals melting at 122° , the β - in tiny, yellow crystals melting at 95 — 96° .

Parachlorobenzophenone yields a white phenylhydrazone melting at 106° , and a yellow diphenylhydrazone melting at 130° . From the ketochloride, uncrystallisable substances only were obtained.

Orthochlorobenzophenone yields only an oily monophenylhydrazone, and the same is the case with the ketochloride.

Chlorobenzile, $\text{CPh} \cdot \text{O} \cdot \text{CPhCl}_2$, yields, with phenylhydrazine, the dihydrazone in yellow crystals melting at 225° . With diphenylhydrazone, it, as well as benzile itself, yields only a monohydrazone in yellow crystals melting at 108° .

For the more general properties of these hydrazones, especially the isomeric ones, reference must be made to the preceding abstract. The formulæ of the two classes of compounds are as below.

CXY:N·NHPh,
Phenylhydrazones.

CXY:N·NPh₂.
Diphenylhydrazones.

C. F. B.

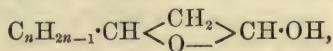
Hexahydrobenzoic acid. By O. ASCHAN (*Ber.*, 25, 3658—3661). The author considers that the differences observed by Markovnikoff (this vol., i, 93) between hexahydrobenzoic acid and "heptanaphthenic acid" are insufficient to prove their isomerism; hexahydrobenzoic acid in alkaline solution is scarcely acted on by potassium permanganate, even in 11½ hours, whilst Δ²-tetrahydrobenzoic acid is immediately oxidised. Markovnikoff's acid probably contained a little Δ¹-tetrahydrobenzoic acid (m. p. 29°), which would account for the different result observed by him.

The reduction of benzoic acid by means of sodium amalgam proceeds slowly, unless pure mercury is employed.

Calcium hexahydrobenzoate is stated by Markovnikoff to crystallise with 5H₂O, whilst the author's analyses indicated 4H₂O; and fresh determinations confirm the previous results; the difference is probably due to the method of drying the salt and to the solvent employed for its purification.

J. B. T.

Acids from Baku Petroleum. By O. ASCHAN (*Ber.*, 25, 3661—3670).—A summary of the author's previous work on this subject (compare Abstr., 1891, 737, and 1892, 1452, 1481) and on hydrobenzoic acids. The lower naphthenecarboxylic acids are not hexamethylene derivatives, and do not belong to the same polymethylene series as the hydrocarbons. Zaloziecki's suggestion (Abstr., 1891, 999), that the carboxylic acids are "lactoalcohols,"



is disproved by the fact that they are not acted on by hydrochloric acid, even when heated with it at 250°, and they have all the properties of acids.

Zaloziecki states that on oxidation with sulphuric acid and potassium dichromate, heptanaphthenecarboxylic acid yields fatty acids of high molecular weight; the author is unable to confirm this, as, under the conditions stated, he obtained acetic and succinic acids in some quantity, together with unchanged heptanaphthenecarboxylic acid and a trace of oxalic acid.

J. B. T.

Orthonitrobenzylmetamidobenzoic acid. By C. PAAL and E. FRITZWEILER (*Ber.*, 25, 3590—3607).—*Orthonitrobenzylmetamidobenzoic acid*, NO₂·C₆H₄·CH₂·NH·C₆H₄·COOH, is prepared by boiling an alcoholic solution of orthonitrobenzyl chloride and metanitrobenzoic acid in molecular proportion for 6—7 hours; the main portion separates on cooling. It forms yellow leaflets, melts at 170—171°, and is insoluble in water. The *potassium* salt crystallises from alcohol in yellow needles, and melts at 196°; its aqueous solution gives precipitates on the addition of barium and calcium chlorides or of salts of the heavy metals. The *ethyl* salt forms small, amber-coloured crys-

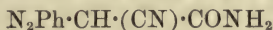
tals, and melts at 100° . The nitro-group in this acid could not be reduced to the amido-group by means of zinc-dust. The *formyl* derivative, $\text{NO}_2 \cdot \text{C}_7\text{H}_5 \cdot \text{N}(\text{COH}) \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, crystallises in brownish, jagged prisms, and melts at 195° ; whilst the *acetyl* derivative forms small, yellowish crystals, and melts at 239° . Both these derivatives yield indazylbenzoic acid (see below) on reduction with tin and hydrochloric acid, or with zinc-dust and acetic acid, together with a compound melting at $156\text{--}157^{\circ}$, but hydrogenised quinazoylbenzoic acids are not produced (compare Abstr., 1892, 81).

Metindazylbenzoic acid, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{N} \\ | \\ \text{CH} \end{smallmatrix} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, is obtained by reducing an alcoholic solution of the nitrobenzylamidobenzoic acid with tin and hydrochloric acid. It crystallises in concentrically grouped, white needles, melts at 211° , and is sparingly soluble in alcohol, benzene, and hot mineral acids. The *hydrochloride* and the acid *sulphate* are dissociated by water; the latter melts at $146\text{--}148^{\circ}$. An aqueous solution of the *sodium* salt gives precipitates with barium and calcium chlorides, and with salts of the heavy metals. The *ethyl* salt melts at 92° .

Orthometazobenzenedicarboxylic acid, $\text{N}_2(\text{C}_6\text{H}_4 \cdot \text{COOH})_2$, is formed by oxidising metindazylbenzoic acid, dissolved in glacial acetic acid, with chromic acid. It crystallises in aggregates of red needles, melts at 237° with decomposition, and is sparingly soluble in alcohol and ether. Aqueous solutions of the *alkali* salts do not give a precipitate with barium chloride until boiled with it. The *hydrazo-acid* is obtained by reducing an ammoniacal solution with zinc-dust; it crystallises in small, almost white needles, melts at 206° with decomposition, and is readily soluble in the ordinary solvents. A solution of the *sodium* salt gives no precipitate with barium chloride, but voluminous precipitates are produced with lead and zinc salts, as also with silver nitrate; the *silver* salt is very unstable. When the azo-acid is reduced with tin and hydrochloric acid, *orthometabenzidinedicarboxylic acid* is formed; it is being further examined. A. R. L.

Ethyl Azobenzenecyanacetate. By F. KRÜCKEBERG (*J. pr. Chem.* [2], 46, 579—580; compare Haller, Abstr., 1888, 823).—This compound may be prepared by the action of diazobenzene chloride on ethyl cyanacetate in presence of sodium acetate; it crystallises in silky needles, and melts at $106\text{--}108^{\circ}$. The *potassium compound*, $\text{C}_{11}\text{H}_{10}\text{KN}_3\text{O}_2 + 2\text{H}_2\text{O}$, was obtained, and from this the other metallic compounds, which are mostly coloured and sparingly soluble, were prepared. When the solution of the potassium compound is treated with excess of acetic or hydrochloric acid, the original compound (m. p. 108°) is obtained; but if the calculated quantity of acid be employed, an *isomeride*, which crystallises in rhombohedra and melts at 82° , is isolated. The isomeride of higher melting point requires 40 times its weight of benzene to dissolve it at the ordinary temperature; the other only requires four times its weight. Warming with hydrochloric acid will also effect the conversion from the higher melting point to the lower; hot acetic anhydride effects the reverse change. The *ethyl* derivative, $\text{N}_2\text{Ph} \cdot \text{CEt}(\text{CN}) \cdot \text{COOEt}$, obtained from the

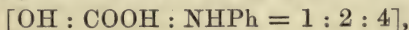
potassium compound and ethyl bromide, forms rhombic crystals, and melts at 72° ; the *benzoyl* derivative crystallises in needles, and melts at 158° . A *dibromo-derivative*, $C_{11}H_9Br_2N_2O_3$, and the *amide*,



(m. p. 245°), were prepared, the latter from both isomerides.

A. G. B.

Anilidosalicylic acid. By R. DIERBACH (*Annalen*, **273**, 117—126).—*Anilidosalicylic acid*, $NHPh \cdot C_6H_3(OH) \cdot COOH$

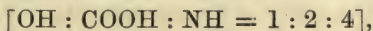


is formed in small quantities, together with dianilidoquinoneanil, azophenine, and resinous products, when diazosalicylic acid is treated with aniline in benzene solution, a very energetic reaction taking place with evolution of nitrogen and carbonic anhydride. It crystallises in colourless needles, melts at 217.5° , is almost insoluble in cold water, and gives a violet coloration with ferric chloride; on distillation with lime, it seems to yield paranilidophenol. The *barium salt*, $(C_{13}H_{10}NO_3)_2Ba + 6H_2O$, is readily soluble in hot, but only sparingly in cold, water, and begins to decompose at 231° . The *sulphate*, $(C_{13}H_{11}NO_3)_2 \cdot H_2SO_4$, crystallises in rose-coloured tufts, and dissolves freely in water and alcohol.

Aniline bromosalicylate, $C_7H_5BrO_3 \cdot NH_2Ph$ $[OH : Br : COOH = 1 : 2 : 4]$, crystallises from hot water in long needles, and melts at 134° .

Bromosalicylanilide, $OH \cdot C_6H_3Br \cdot CO \cdot NHPh$, is formed when aniline bromosalicylate is treated with phosphorus trichloride and the mixture heated at 170° ; it crystallises from alcohol in long needles, melts at 222° , and is soluble in soda.

Dinitranilidosalicylic acid, $COOH \cdot C_6H_3(OH) \cdot NH \cdot C_6H_3(NO_2)_2$

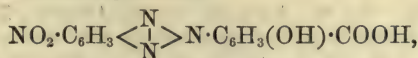


can be obtained by heating an alcoholic solution of amidosalicylic acid with dinitrochlorobenzene at 130° ; it crystallises in slender, red needles, melts at 272° , and dissolves in alkalis with a dark red coloration.

Diamidanilidosalicylic acid, $COOH \cdot C_6H_3(OH) \cdot NH \cdot C_6H_3(NH_2)_2$, prepared by reducing the preceding compound with stannous chloride, is a colourless substance, but its solutions in alkalis quickly turn deep blue, and its acid solutions reddish. The *sulphate* crystallises in rose-coloured needles.

Nitramidanilidosalicylic acid, $COOH \cdot C_6H_3(OH) \cdot NH \cdot C_6H_3(NH_2) \cdot NO_2$, is obtained when the dinitranilido-acid is reduced with ammonium sulphide; it forms red crystals, and is soluble in acids.

Nitrophenylazimidosalicylic acid,



is formed when the preceding compound is treated with amyl nitrite and hydrochloric acid in alcoholic solution; it crystallises in colourless needles, and melts at 269° with decomposition. F. S. K.

The Stereoisomeric Isopropylphenylglycollic acids. By M. FILETI (*J. pr. Chem.* [2], **46**, 560—563).—These acids are separated by means of quinine and cinchonine. By recrystallising the quinine salts from aqueous alcohol, the lævorotatory acid is obtained pure, but the dextrorotatory acid cannot be freed from the lævorotatory. On the other hand, when the cinchonine salts are recrystallised, the dextrorotatory acid is obtained pure. Both acids crystallise in thick tables which melt at 153—154°, whereas the inactive mixture forms laminæ, and melts at 156—157°. 100 parts of absolute alcohol at 13° dissolve 47·49 parts of the dextrorotatory acid, 47·32 of the lævorotatory, and 21·61 of the inactive. For the dextro-acid, $[\alpha]_D = 134·9^\circ$ ($c = 4·0568$, $l = 2$, $t = 17^\circ$, $\alpha = 10·95^\circ$); for the lævo-acid, $[\alpha]_D = -135^\circ$ ($c = 4·0916$, $l = 2$, $t = 17^\circ$, $\alpha = -11·05^\circ$). Both acids lose their activity when heated with water in a sealed tube at 180—200° for 40 hours. The lævo-quinine salt crystallises in needles, and melts at 204—205°; the dextro-quinine salt forms slender needles, and melts at 192—193°; the dextro-cinchonine salt crystallises in long, lustrous needles, and melts at 201°; the lævo-cinchonine salt also forms needles, and melts at 167°; the solubility and rotation of these salts are given.

When either of these acids is treated with saturated hydrochloric acid, it is converted into inactive isopropylphenylchloroacetic acid, which is immediately decomposed by water, and by treatment with soda, yields inactive isopropylphenylglycollic acid. A. G. B.

Derivatives of Homoterephthalic acid. By M. FILETI and E. CAIROLA (*J. pr. Chem.* [2], **46**, 563—564).—*Nitrohomoterephthalic acid* $[\text{COOH} : \text{NO}_2 : \text{CH}_2\text{COOH} = 1 : 3 : 4]$, the product of the nitration of homoterephthalic acid, crystallises in straw-coloured tables, melts at 222—223°, and dissolves in hot water and alcohol, but sparingly in the other ordinary solvents. The *methyl salt* is colourless, and melts at 75—77°; excess of ammonia imparts an amethyst colour to its alcoholic solution. When the acid is heated with alcoholic ammonia at 120°, it is split up into carbonic anhydride and metanitroparatoluic acid (m. p. 189°); treatment of the chloride of this acid with ammonia yields *metanitrotoluamide*, which crystallises in long, yellow needles, melts at 165—166°, and is sparingly soluble.

Oxindolecarboxylic acid, $\text{COOH} \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \end{smallmatrix} > \text{CO}$, is the product of the reduction of nitrohomoterephthalic acid by ammonium sulphide; it forms yellow crystals, melts at 313°, and is sparingly soluble. Its *ammonium salt*, with 2 mols. H_2O , and *barium salt*, with $3\frac{1}{2}$ mols. H_2O , were prepared. A. G. B.

Chebolic acid. By W. ADOLPHI (*Arch. Pharm.*, **230**, 684—705).—This acid is obtained from myrobalans, the fruits of *Terminalia chebula*, best in the following manner:—The dried fruits are powdered, macerated for 10 days at the ordinary temperature with 90 per cent. alcohol, pressed, and filtered. The alcohol is completely removed from the extract, and the residue then dissolved in hot

water; cold water is added until no further milkiness appears, and the whole is allowed to settle, and then filtered. To the filtrate, sodium chloride is added until a permanent turbidity appears, and the solution is then shaken out with ethyl acetate, which dissolves chebolic and tannic acids. To remove the latter, the ethyl acetate is distilled off, and the residue dissolved in water, and shaken out with ether; from the aqueous solution, crystals of chebolic acid then separate on standing, and may be recrystallised from hot water. The yield is 3.5 per cent.

Chebolic acid, $C_{28}H_{24}O_{19} + H_2O$, begins to melt at about 200° , and is optically active, having $[\alpha]_D = +66.94^\circ$. The molecular weight of the anhydrous compound was determined by Beckmann's boiling-point method in acetone solution. The acid seems to be monobasic and forms an amorphous *barium salt*, $(C_{28}H_{23}O_{19})_2Ba$, which is white when moist, and green when dry, and a grey, amorphous, basic (?) *zinc salt*, probably $(C_{28}H_{23}O_{19})_2Zn + ZnO$. These salts appear, in general, to be decomposed by water, even in the cold. With strychnine, an acid salt, $C_{19}H_{22}N_2O_2 \cdot 2C_{28}H_{24}O_{19}$, is formed. With benzoic chloride and soda, a yellowish, amorphous *benzoyl derivative*, $C_{28}H_{20}Bz_4O_{17}$, melting at 88.5° , is obtained. With phenylhydrazine, chebolic acid yields a derivative in the form of a reddish powder, which melts at 142° , and, when dissolved in alcohol and treated with strong aqueous potash, yields a momentarily green, then mulberry-red, and, finally, brownish-red coloration. (Tannic acid, similarly treated, gives a green colour, only gradually changing to red; gallic acid, an immediate red coloration.) When chebolic acid is dissolved in alcohol and the solution saturated with gaseous hydrogen chloride, some ethyl gallate is formed, and, in addition, a yellow, amorphous acid, somewhat analogous in its properties to tannic acid. Sulphuric acid hydrolyses chebolic acid to gallic acid and other undetermined products.

C. F. B.

A Derivative of Amidoacetal. By W. MARCKWALD and A. ELLINGER (*Ber.*, 26, 98—100).—*Dibenzenesulphodihydroaldine*, $SO_2Ph \cdot N < \begin{smallmatrix} CH:CH \\ CH:CH \end{smallmatrix} > NSO_2Ph$, is obtained by shaking benzenesulpho-amidoacetal, $SO_2Ph \cdot NH \cdot CH_2 \cdot CH(OEt)_2$, with concentrated hydrochloric acid and then warming the mixture on the water-bath. It separates from hot alcohol in white crystals, melts at 163° , and is sparingly soluble. When reduced with sodium in boiling amyl alcohol, it is converted into diethylenediamine.

E. C. R.

Acetylnitrocarbazole. By G. MAZZARA and E. LEONARDI (*Gazzetta*, 22, ii, 443—444).—The nitrocarbazole melting at 209 — 210° (*Abstr.*, 1891, 576) yields an *acetyl derivative* which crystallises in yellowish, thin needles melting at 237 — 238° (corr.); it is soluble in chloroform or toluene and sparingly so in alcohol or light petroleum. The same acetylnitrocarbazole (compare *Abstr.*, 1892, 616) is obtained on nitrating acetylcarbazole in acetic acid solution.

W. J. P.

Condensation of Ketones with Phenols. By A. DIANIN (*J. Russ. Chem. Soc.*, **23**, 488—517, 523—546, 601—611).—Acetone (220 grams) was mixed with phenol (1600 grams) and glacial acetic acid (1800 grams), and to this mixture, fuming hydrochloric acid of sp. gr. 1.19 (600 c.c.) was added, the whole being heated in a stoppered vessel for 24 hours at 40—50°. On cooling, crystals separated, and, after these had been collected on an asbestos filter, the filtrate was again heated as before, the treatment being repeated until no more crystals were obtained from the filtrate on further heating. The total weight of the crystalline product was 750—800 grams on each occasion, from which 700 grams of the purified substance was obtained, after distilling off the phenol with steam, and recrystallising from hot 30 per cent. acetic acid. The crystals, on analysis, gave numbers corresponding with the formula $C_{15}H_{16}O_2$, and were proved to be *dimethyldiphenoxymethane*, $CMe_2(C_6H_4\cdot OH)_2$, formed by the condensation of acetone and phenol.

Dimethyldiphenoxymethane is soluble in 2820 parts of water at the ordinary temperature, and in 130 parts at the boiling point. It is easily soluble in alcohol, ether, acetic acid, and alkalis. From hot saturated aqueous solutions, it crystallises in feathery needles, and from dilute solutions in microscopic prisms, or sometimes in what appear to be quadratic plates. Its melting point is 151—152°, and, on boiling, it decomposes, giving off phenol. With ferric chloride, it gives a pale violet coloration, which disappears rapidly, and the green solution in concentrated sulphuric acid also changes to violet on the addition of ferric chloride. The *dibenzoyl* compound, $C_{15}H_{14}O_2Bz_2$, melts at 153—155°; it is not attacked by aqueous potash, but is decomposed by alcoholic potash. The *dimethyl ether*, $CMe_2(C_6H_4\cdot OMe)_2$, is prepared by boiling the diphenol (50 grams) with potash (30 grams) and methyl iodide (65 grams) in methyl alcohol solution for 10 hours with a reflux condenser. It crystallises in the rhombic system, is easily soluble in alcohol and ether, melts at 60.5°, and boils without decomposition at 371°.

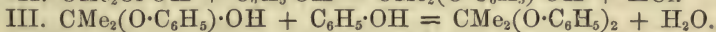
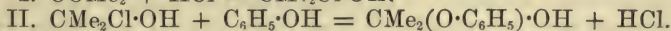
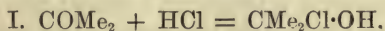
Diethyldiphenoxymethane, $CEt_2(C_6H_4\cdot OH)_2$, was prepared by heating, in a sealed tube, diethyl ketone (63 grams), phenol (374 grams), and hydrochloric acid, sp. gr. 1.19 (70 grams), with continued shaking, for 24 hours at 80—90°. About 80 grams of crude crystalline product was obtained, and this, on repeated recrystallisation from 25 per cent. alcohol, gave needles melting at 198—200°. It is almost insoluble in water, but dissolves readily in ether, alcohol, and alkalis. Fusion with alkali, or heating at 100° with fuming hydrochloric acid, gives paramylphenol, $C_5H_{11}\cdot C_6H_4\cdot OH$. The *dibenzoyl* compound melts at 162.5°.

Dipropyldiphenoxymethane, $CPr_2(C_6H_4\cdot OH)_2$.—Butyrone (1 part) was heated for 30 hours at 60° with phenol (4 parts) and hydrochloric acid, sp. gr. 1.19 (1 part). 18 grams of butyrone gave 10 grams of crude product, which was purified by recrystallisation from dilute alcohol. It melts at 155°, crystallises in needles, and resembles the diethyl compound in its solubility relations. Fuming hydrochloric acid at 100° converts it into heptylphenol. The *dibenzoyl* compound melts at 144—145°.

Methylhexyldiphenoxymethane, $C_6H_{13} \cdot CMe(C_6H_4 \cdot OH)_2$, was prepared from methyl hexyl ketone (20 grams), phenol (80 grams), and fuming hydrochloric acid (20 grams), by heating for 24 hours at $80-90^\circ$. The product was washed several times with warm water to remove phenol and hydrochloric acid, and afterwards distilled with steam, which removed the unattacked methyl hexyl ketone. The residue was then dissolved in benzene and precipitated by petroleum, when it came down as an oil, which crystallised in the course of a fortnight. The pure substance is soluble in alcohol, ether, benzene, glacial acetic acid, and alkalis. Water precipitates it from the acetic acid solution in the form of fine, silky needles melting at 83.5° . Heating with fuming hydrochloric acid for 36 hours at 100° gives octyl phenol. The dibenzoyl compound melts at 114° .

When phenol is oxidised in acid solution by means of potassium permanganate, the diphenol formed, $OH \cdot C_6H_4 \cdot C_6H_4 \cdot OH$, is a di-para-compound. Similarly, the compounds above described are also di-para-compounds, as was proved by the author, who found anisic acid amongst their products of oxidation by means of chromic acid.

With regard to the conditions of the reaction of phenols with ketones, the author finds that $50-60^\circ$ is the most favourable temperature, as at 100° a considerable quantity of tarry matter is formed. A very small quantity of fuming hydrochloric acid can effect the condensation, and even dilute acid (4 per cent.) is not without action. Under the same conditions, the reaction goes more slowly, the greater the molecular weight of the ketone employed; the rate of decomposition of the product by heating with fuming hydrochloric acid proceeds in the inverse order. As to the mechanism of the reaction, the author is inclined to assume the following phases:—



The substance $\text{CMe}_2(\text{OC}_6\text{H}_5)_2$ then undergoes an isomeric transformation into $\text{CMe}_2(\text{C}_6\text{H}_4 \cdot \text{OH})_2$.

The dialkyldiphenoxymethanes, when fused with potash or heated with fuming hydrochloric acid, are decomposed according to the equation $R_2C(C_6H_4 \cdot OH)_2 + H_2O = R_2CH \cdot C_6H_4 \cdot OH + C_6H_4(OH)_2$.

The dihydroxybenzene might be expected to be quinol, but a large quantity of tar and of amorphous coloured substances are always formed, probably as products of the interaction of the quinol with the original diphenol.

1:4-*Isopropylphenol*.—Fuming hydrochloric acid has no action on dimethyldiphenoxymethane, but fusion with potash yields 1:4-isopropylphenol, which melts at 61° , boils at $227-228^\circ$, and is identical with that prepared by Paternò and Spica.

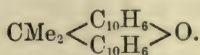
1:4-*Amylphenol*, $\text{CHEt}_2 \cdot C_6H_4 \cdot \text{OH}$, may be prepared from the diethyl-diphenol, either by fusion with potash or by the action of fuming hydrochloric acid. It is easily soluble in ether, alcohol, and acetic acid; from either of the latter it may be precipitated by the addition

of water in the form of fine, silky needles. It melts at $79.5-80^{\circ}$, and distils without decomposition at 253° . Ferric chloride gives no coloration. In strong alkaline solution, it only dissolves with difficulty, although it is easily soluble in weak alkalis. The benzoyl compound melts at $54-55^{\circ}$.

1: 4-Heptylphenol, $\text{CHPr}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$.—Butyrone (1 part), phenol (4 parts), and hydrochloric acid (sp. gr. 1.19, 3 parts) were heated for 48 hours at 100° . The product was washed with water and distilled over with steam; the oil thus obtained was treated with 2 per cent. potash solution, from which the dissolved phenol was liberated by a stream of carbonic anhydride, and again subjected to distillation with steam. Heptylphenol has a pleasant odour, is insoluble in water, and easily soluble in alcohol, ether, and acetic acid. It is volatile with steam, melts at $70-71^{\circ}$, and boils at 281° . The benzoyl compound melts at $29.5-30^{\circ}$, and the methyl ether distils at $267-268^{\circ}$, its sp. gr. at $0^{\circ}/4^{\circ}$ being 0.9349.

1: 4-Octylphenol, $\text{C}_8\text{H}_{17} \cdot \text{CHMe} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, may be prepared, similarly to heptylphenol, from methyl hexyl ketone. It is a liquid having an unpleasant odour, and closely resembling in its properties the compounds above described. The benzoyl compound is also liquid.

The author found that α -naphthol condenses readily with acetone to give the compound α -oxydinaphthylenedimethylmethane,

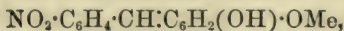


Acetone (1 mol.) and α -naphthol (2 mols.) were dissolved in glacial acetic acid, and to the solution was added as much fuming hydrochloric acid as possible without occasioning the precipitation of the naphthol. The mixture was heated in a stoppered bottle at $80-100^{\circ}$ until the contents solidified to a dense, crystalline mass. The crystals were pressed and recrystallised, first from alcohol and then from acetic acid. From ether, the substance crystallises in four-sided, almost quadratic, plates, which melt at 186° , and are always coloured slightly pink.

J. W.

Condensation Products of Dimethylresorcinol and Methylresorcinol with the Nitrobenzaldehydes. By M. ZENONI (*Gazzetta*, 22, ii, 298—303; compare *Abstr.*, 1891, 620, *et seq.*).—*Metanitrophenylmetadimethoxyphenylmethane*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}_6\text{H}_2(\text{OMe})_2$, is obtained by heating dimethylresorcinol and metanitrobenzaldehyde with dilute sulphuric acid. It forms a yellow powder which begins to decompose at $158-160^{\circ}$, and does not melt; it is very soluble in ethyl acetate, less so in acetic acid, and only sparingly in benzene, light petroleum, and carbon bisulphide. The *para*-isomeride has very similar properties, but the *ortho*-compound is unstable.

Metanitrophenylmetahydroxymethoxyphenylmethane,



is obtained as a yellow powder by heating metanitrobenzaldehyde and

methylresorcinol with dilute sulphuric acid. It resembles the substances described above, and begins to decompose at 150°.

W. J. P.

Xanthone Derivatives and Orthocresotic Anhydride. By M. SCHÖPFF (*Ber.*, **25**, 3642—3647).—4-Methylxanthone,



is obtained, together with dimethylxanthone, by the distillation of phenyl orthocresotate. It is more soluble in alcohol than dimethylxanthone, and is separated by precipitating the alcoholic mother liquors with dilute soda. It crystallises in colourless needles, melts at 105°, boils at 350—355°, and, with sulphuric acid, gives a yellow solution, which exhibits a bluish-green fluorescence.

4:5-Dimethylxanthone crystallises in colourless needles, and melts at 171—172°. It is more easily obtained by the distillation of orthocresyl orthocresotate, and comes over at 350—360°. It is obtained, together with orthocresotic anhydride, by heating orthocresotic acid and acetic anhydride in a reflux apparatus, and then distilling the product.

Orthocresotic anhydride, $(\text{C}_8\text{H}_6\text{O}_2)_2$, is a white, crystalline powder; it melts at 224—225°, is very sparingly soluble in most solvents, insoluble in alkaline carbonates, and when boiled with caustic alkalis, slowly dissolves, and is converted into orthocresotic acid.

4:5-Xanthonedicarboxylic acid, $\text{COOH} \cdot \text{C}_6\text{H}_3 < \overset{\text{CO}}{\underset{\text{O}}{\text{C}}} > \text{C}_6\text{H}_3 \cdot \text{COOH}$, is obtained by oxidising dimethylxanthone with potassium permanganate. It crystallises in beautiful, white needles, does not melt at 285°, and dissolves in concentrated sulphuric acid with a yellow coloration and a pale, bluish-green fluorescence.

E. C. R.

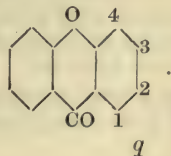
Constitution of the Monhydroxyxanthenes. By E. DREHER and S. v. KOSTANECKI (*Ber.*, **26**, 71—78; compare *Abstr.*, 1892, 1096, 1097, 1099).—Graebe has shown that α -hydroxyxanthone is a true hydroxy-derivative of xanthone, since it yields methylenediphenylene oxide on distillation with zinc-dust; the authors find that when β -hydroxyxanthone is distilled with zinc-dust, it is converted into xanthene (m. p. 96°) which, on oxidation, yields xanthone; 4-hydroxyxanthone* shows the same behaviour.

1-Hydroxy-2:4-dimethylxanthone, $\text{C}_{13}\text{H}_5\text{O}_2\text{Me}_2 \cdot \text{OH}$, is obtained, together with xanthone, when a mixture of metaxylo-orscinol,



salicylic acid, and acetic anhydride is distilled; it crystallises in long,

* The following system of numbering is adopted



yellow needles, melts at about 160° , and forms an intensely yellow sodium derivative which is insoluble in boiling water.

From its method of formation, this compound must have the constitution assigned to it, that is to say, the hydroxyl group is in the 1-position; the hydroxyl group in α -hydroxyxanthone and in α -hydroxymethylxanthone, both of which resemble hydroxydimethylxanthone very closely in properties, is therefore in the 1-position, whereas in β -hydroxyxanthone it is in the 3-position.

Orthodioxanthone, $C_{20}H_{10}O_4$, is formed in the preparation of 4-hydroxyxanthone from salicylic acid and catechol (*loc. cit.*); it crystallises from glacial acetic acid in long, colourless needles, melts at 317° , and dissolves in concentrated sulphuric acid, yielding a yellow solution which shows a greenish fluorescence.

The properties of the four monhydroxyxanthenes can be readily accounted for and brought into agreement with the above view of their constitution; the differences in colour which they exhibit are due to the difference in the position of the hydroxyl group relative to the chromophore CO.

Experiments on the behaviour of the hydroxyxanthenes on treatment with methyl iodide and alcoholic potash have shown that 1-hydroxyxanthone cannot be converted into its methyl derivative, whilst the methyl derivatives of the other monhydroxyxanthenes are easily obtained.

2-*Methoxyxanthone*, $C_{14}H_{10}O_3$, crystallises from alcohol in colourless needles, and melts at 131.5° ; its solution in concentrated sulphuric acid shows a yellowish-green fluorescence.

3-*Methoxyxanthone* crystallises from alcohol in colourless needles, melts at 128.5° , and its solution in sulphuric acid shows a bluish fluorescence.

4-*Methoxyxanthone* forms colourless needles, and melts at 165° ; it dissolves in sulphuric acid, yielding a yellow solution.

1-*Hydroxy-3-methoxyxanthone*, $OH \cdot C_{13}H_6O_2 \cdot OMe$, is formed when isoeuxanthone is heated with methyl iodide and alcoholic potash; it crystallises from glacial acetic acid in needles, melts at 145° , and forms a sparingly soluble sodium derivative very similar to that of 1-hydroxyxanthone.

F. S. K.

Preparation of Hydroxyxanthenes from the Salols of Polyhydric Phenols. By W. BAUMEISTER (*Ber.*, 26, 79—82).—*Disalicylresorcinol*, $C_6H_4(O \cdot CO \cdot C_6H_4 \cdot OH)_2$, can be obtained by heating resorcinol with salicylic acid; it crystallises in colourless needles, and melts at 111° ; when heated for some hours, and then distilled, it yields 1-hydroxyxanthone, 3-hydroxyxanthone, xanthone, and a di-xanthone melting at 256° , and identical with the compound described by Kostanecki and Seidmann (*Abstr.*, 1892, 1097).

Disalicylquinol, $C_{20}H_{14}O_4$, prepared by heating a mixture of quinol and salicylic acid with phosphorus oxychloride, crystallises in colourless needles melting at 148° ; on distillation, it yields xanthone and 2-hydroxyxanthone.

Dinaphthosalicylresorcinol, $C_{26}H_{18}(O \cdot CO \cdot C_{10}H_6 \cdot OH)_2$, obtained in like manner from β -naphtholcarboxylic acid, crystallises in needles melting

at 232—233°; on distillation, it yields hydroxyphenonaphthoxanthone (compare Kostanecki, Abstr., 1892, 1099) and γ -dinaphthoxanthone.

F. S. K.

Condensations with Potassium Cyanide. By A. SMITH (*Ber.*, 26, 60—65; compare Chalanay and Knoevenagel, Abstr., 1892, 619).—Desylacetophenone is formed, together with a considerable quantity of a very sparingly soluble substance, when a solution of benzoin and acetophenone in dilute alcohol is boiled with a small quantity of potassium cyanide; the sparingly soluble product combines directly with bromine, and seems to consist of a mixture of two or more, possibly isomeric, compounds.

A compound of the constitution



which the author names *phenacyldesoxycuminoïn*, is formed, together with other substances, when cuminoïn is treated with acetophenone and potassium cyanide under the conditions mentioned above; it crystallises in colourless needles, and melts at 145°.

Phenacyldesoxypiperonoïn,



obtained from piperonoïn and acetophenone in like manner, melts at 155°.

$\alpha\beta$ -*Dicumyl- α' -phenylfurfuran*, $\text{C}_{28}\text{H}_{28}\text{O}$, is formed when phenacyldesoxycuminoïn is dissolved in concentrated sulphuric acid; it crystallises from dilute alcohol in colourless plates melting at 85°. The *hydrazone*, $\text{C}_{34}\text{H}_{34}\text{N}_2$, prepared by treating phenacyldesoxycuminoïn with phenylhydrazine in glacial acetic acid solution, crystallises in colourless needles, and melts at 162—163°; its constitution was not determined.

F. S. K.

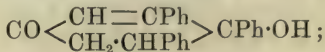
Condensation of Acetone with Benzoin by means of Potassium Cyanide. By A. SMITH (*Ber.*, 26, 65—71).—*Ketohydroxytriphenyltetrahydrobenzene*, $\text{C}_{24}\text{H}_{20}\text{O}_2$, is produced when a solution of benzoin and acetone in dilute alcohol is heated with a small quantity of potassium cyanide; it crystallises from glacial acetic acid in long, colourless needles, melts at 248°, and is identical with the compound obtained by Japp and Raschen (*Trans.*, 1890, 783), but to which they assigned the composition $\text{C}_{34}\text{H}_{28}\text{O}_3$. The *oxime*, $\text{C}_{24}\text{H}_{21}\text{NO}_2$, is obtained when the ketobenzene derivative is treated with hydroxylamine hydrochloride in alcoholic solution; it crystallises in colourless needles, and melts at 233—234°. The *hydrazone*, $\text{C}_{30}\text{H}_{26}\text{N}_2\text{O}$, crystallises in yellow needles melting at 197°.

Acetyltriphenylphenol, $\text{C}_6\text{H}_5\text{Ph}_3\cdot\text{OAc}$ [$\text{OAc} : \text{Ph}_3 = 1 : 3 : 4 : 5$], is formed when the ketobenzene derivative is boiled with acetic anhydride and a trace of zinc chloride; it crystallises in long, colourless needles, melts at 189°, and is converted into triphenylphenol on hydrolysis with alcoholic potash.

Triphenylphenol, $\text{C}_{24}\text{H}_{18}\text{O}$, separates from alcohol in thick needles, melts at 226°, and is insoluble in potash; on distillation with zinc-

dust, it yields a *triphenylbenzene* which melts at 157° , and has probably the constitution $[\text{Ph}_3 = 1 : 2 : 3]$.

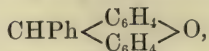
Ketohydroxytriphenyltetrahydrobenzene can also be obtained by the condensation of benzoin with benzalacetone in presence of potassium cyanide; this fact, and the reactions described above, show that its constitution is probably represented by the formula



it is also formed, together with a compound melting at 110 — 112° , probably desylmesityl oxide, when benzoin is treated with mesityl oxide in presence of potassium cyanide.

F. S. K.

The Fluorescein Group. By R. MEYER and E. SAUL (*Ber.*, **25**, 3586—3590).—The compound obtained by distilling hydrofluoric acid with soda-lime and zinc-dust (Abstr., 1892, 1228) is diphenylenephylmethane, $\text{CHPh} < \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} >$ (m. p. 145°). When fluoran is distilled with zinc-dust, *diphenylenephylmethane oxide*,



is obtained; it crystallises in large rhombohedra, melts at 135 — 137° , and dissolves readily in ether and benzene, the solutions not exhibiting fluorescence. A second compound, $\text{C}_{20}\text{H}_{12}\text{O}$, may also be isolated; it crystallises in golden-yellow leaflets, melts at 150 — 152° , dissolves in ether, forming a solution which exhibits a strong, green fluorescence; and is probably a phenylanthranol. A third compound was also produced in the interaction, but its amount was so small that it precluded its examination. Fluoran and diphenylphthalide yield crystalline derivatives with phenylhydrazine; these are being investigated.

A. R. L.

Action of Bleaching Powder and of Hypochlorous acid on Quinones. By T. ZINCKE (*Ber.*, **25**, 3599—3607; compare Abstr., 1892, 720, 857, and 859).—These experiments relate to α -naphtha-

quinone. *$\alpha\alpha$ -Diketotetrahydronaphthalene oxide*, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CO} \cdot \text{CH} \\ | \\ \text{CO} \cdot \text{CH} \end{array} > \text{O}$, is

obtained by mixing α -naphthaquinone with an excess of bleaching powder solution; after a while the mixture becomes warm, and at the end of 24 hours the flocculent, white product is collected, washed, and crystallised from 50 per cent. acetic acid, when it separates in long, white needles, melts at 136° , and is sparingly soluble in ether. Isonaphthazarin (Abstr., 1892, 494 and 720) is formed when it is heated with water at 130 — 140° , whilst hydroxy- α -naphthaquinone is produced on treatment with aqueous alkalis. The last-named compound is obtained together with chlorhydroxy- α -naphthaquinone when the oxide is heated with dilute hydrochloric acid. *Chlorhydroxyhydro- α -naphthaquinone* (m. p. 142 — 143°) is furnished on boiling the oxide, dissolved in 50 per cent. acetic acid, with stannous chloride and hydrochloric acid. When an excess of aniline is added

to an alcoholic solution of the oxide, *anilidohydroxydiketotetrahydronaphthalene*, $C_6H_4 < \begin{smallmatrix} CO \cdot CH \cdot OH \\ CO \cdot CH \cdot NHPh \end{smallmatrix}$, is obtained, together with Plagemann's anilidohydroxy- α -naphthaquinone (m. p. 210°). The former crystallises in needles of a golden lustre, and is converted into the latter when boiled with alcohol. Attempts to prepare the anilidohydroxyquinone from isonaphthazarin were unsuccessful, but when the former is heated with bromine and acetic acid, it is converted into tribromaniline and isonaphthazarin, a fact which favours the view that the latter is a derivative of α -naphthaquinone. When $\alpha\alpha$ -diketotetrahydronaphthaquinone oxide is dissolved in 50 per cent. acetic acid, and treated with aniline, *hydroxy- α -naphthaquinoneanilide*, $C_6H_4 < \begin{smallmatrix} CO - C \cdot NHPh \\ C(NPh) \cdot CH \end{smallmatrix}$, a blue compound melting at 240°, is obtained; whilst if the reaction be conducted in glacial acetic acid solution, anilido- α -naphthaquinoneanilide (m. p. 190°) is an accompanying product.

A. R. L.

Derivatives of the β -Naphtholcarboxylic acid melting at 216°. By N. ROSENBERG (*Ber.*, 25, 3634—3635).—*Ethyl β -hydroxynaphthoate* crystallises in radiating needles, melts at 85°, boils at 290—291° without decomposition, and gives a dark green coloration with ferric chloride.

β -Hydroxynaphthamide, $OH \cdot C_{10}H_6 \cdot CONH_2$, is obtained by heating the ethyl salt with alcoholic ammonia at 170°. It separates from acetic acid in beautiful crystals, and melts at 185°.

β -Hydroxynaphthomethylanilide, $OH \cdot C_{10}H_6 \cdot CO \cdot NMePh$, is obtained by adding phosphorus trichloride to a mixture of β -naphtholcarboxylic acid and methylaniline. It melts at 150°, and gives a green coloration with ferric chloride.

E. C. R.

α -Naphtholsulphonic acids. By M. CONRAD and W. FISCHER (*Annalen*, 273, 102—117).—The authors have examined the products of the direct sulphonation of α -naphthol, in order to clear up various conflicting statements relative to the nature and properties of the acids so formed.

When α -naphthol is heated at 50° for two hours with concentrated sulphuric acid (2 parts), the principal product is α -naphtholdisulphonic acid [$OH : (SO_3H)_2 = 1 : 2 : 4$], only a small quantity of the monosulphonic acid [$OH : SO_3H = 1 : 2$] being formed.

When a solution of α -naphthol (2 parts) in glacial acetic acid (1 part) is heated for about an hour with concentrated sulphuric acid (2 parts) at 45—50°, about half of the α -naphthol is not acted on, the remainder being for the most part converted into a mixture of 1 : 2- and 1 : 4-naphtholsulphonic acids, which can be readily separated by means of their potassium salts.

Potassium 1 : 2-naphtholsulphonate, $OH \cdot C_{10}H_6 \cdot SO_3K + \frac{1}{2}H_2O$, crystallises from water in lustrous prisms, and is only very sparingly soluble in boiling alcohol; 100 parts of water at 18° dissolve about 2.7 parts of the salt, but on the addition of sodium chloride, potassium

chloride, &c., the organic salt is almost completely precipitated. The sodium salt crystallises in prisms or needles, and is soluble in boiling alcohol. The barium salt and the lead salt both crystallise with 1 mol. H_2O .

Potassium nitrosonaphtholsulphonate $[\text{O} : \text{SO}_3\text{K} : \text{NOH} = 1 : 2 : 4]$ forms dark red crystals, and its aqueous solution gives a reddish-brown precipitate with ferric chloride; on treatment with warm dilute nitric acid, it yields dinitronaphthol. The corresponding silver salt has the composition $\text{C}_{10}\text{H}_6\text{NO}_2 \cdot \text{SO}_3\text{Ag} + \text{H}_2\text{O}$. The aniline salt is a yellow, crystalline compound; when heated with aniline at 130 – 140° , it gives a dark red, crystalline substance, probably naphthaquinonedianilide, which melts at 180° , and has the composition $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}$.

Amidonaphtholsulphonic acid $[\text{OH} : \text{SO}_3\text{H} : \text{NH}_2 = 1 : 2 : 4]$, prepared by reducing the nitroso-acid, crystallises in needles, and is identical with the compound described by Seidel (Abstr., 1892, 721).

The alkali salts of 1 : 4 naphtholsulphonic acid are readily soluble in water, and are not precipitated from the solution on adding potassium chloride or alcohol. When a few particles of the potassium salt are treated with cold dilute nitric acid, it yields a dark red solution at first, but afterwards a dark flocculent precipitate is formed; the potassium salt of the 1 : 2-acid, under the same conditions, gives a transient blood-red solution, from which a yellow, resinous substance quickly separates.

The potassium salt of nitrosonaphtholsulphonic acid obtained from the 1 : 4-sulphonic acid crystallises in yellow plates, and is readily soluble in hot water; the corresponding silver salt, $\text{C}_{10}\text{H}_6\text{NO}_5\text{SAg}$, separates from hot water in crystals.

F. S. K.

Dinaphthoxanthen (Methylenedinaphthylene Oxide). By W. WOLFF (*Ber.*, 26, 83–86).—Dihydroxy- β -dinaphthylmethane, $\text{CH}_2(\text{C}_{10}\text{H}_6\text{OH})_2$, can be obtained by adding 40 per cent. formaldehyde to a solution of β -naphthol in a mixture of dilute hydrochloric acid and alcohol; it melts at 194° , not at 188 – 189° , as stated by Abel (this vol., i, 172). The diacetyl derivative, $\text{C}_{25}\text{H}_{20}\text{O}_4$, crystallises in colourless needles, and melts at 211° .

Dinaphthoxanthen, $\text{CH}_2 < \text{C}_{10}\text{H}_6 > \text{O}$, is formed when the preceding compound is heated with toluene and phosphorus oxychloride at 110° ; it crystallises in colourless needles, or prisms, melts at 199° , and dissolves in concentrated sulphuric acid, yielding a yellowish-green solution, which shows a green fluorescence.

Tetrahydroxydinaphthylmethane, $\text{CH}_2[\text{C}_{10}\text{H}_6(\text{OH})_2]_2$, prepared by treating dihydroxynaphthalene $[(\text{OH})_2 = 2 : 7]$ with formaldehyde and dilute hydrochloric acid, crystallises in colourless needles, turns brown at 230° , and melts at 252° with decomposition; it dissolves in concentrated sulphuric acid, yielding a yellow solution, which quickly turns red on exposure to the air. The tetracetyl derivative, $\text{C}_{29}\text{H}_{24}\text{O}_8$, crystallises in needles, and melts at 249.5° .

F. S. K.

Action of Sulphuric acid on Citrene. By G. BOUCHARDAT and J. LAFONT (*Compt. rend.*, **115**, 1083—1085).—When 146 grams of monhydrated sulphuric acid is added gradually to 1330 grams of citrene (b. p. 175—178°; $[\alpha]_D = +72.40$) there is at first considerable development of heat, and the liquid must be cooled, but the addition of the second half of the acid does not increase the temperature of the mixture. After remaining for 24 hours, only very minute quantities of sulphurous anhydride are given off, but the whole of the citrene has disappeared, and the products are optically inactive. On washing with water, it is found that 140 grams of the sulphuric acid out of the 146 remain in the free state, and the water contains no sulphonc acid. The product contains cymene and a hydrocarbon which seems to be pseudocumene, both of which probably pre-exist in the citrene, but the greater part boils at 310—320°, and consists of diterpilene or colophene. There is also a residue which solidifies when cold, and which consists of higher polymerides of citrene. It follows that the action of sulphuric acid on citrene furnishes solely higher polymerides of that hydrocarbon, the most abundant being diterpilene. This result explains the formation of diterpilene in the preparation of terebene or inactive camphene. One of the products of the action of sulphuric acid on terebenthene is a lævograte terpilene boiling at 178°, and physically isomeric with citrene, and probably this terpilene, by the action of further quantities of sulphuric acid, is converted into an inactive diterpilene, identical with that derived from citrene.

C. H. B.

A Crystalline Dihydrochloride from Eucalyptus Oil. By ANTHOINE (*J. Pharm.* [5], **26**, 391—394).—By acting with gaseous hydrogen chloride on those portions of eucalyptus oil which boil between 150° and 178°, a crystalline dihydrochloride, $C_{10}H_{16}, 2HCl$, is obtained, which melts at 50°, boils at 115°, and has properties similar to those of the dihydrochloride obtained from oil of turpentine. Small amounts act as antiseptics to putrescible solutions, but do not hinder the action of enzymes.

T. G. N.

American Menthol. By J. H. LONG (*J. Amer. Chem. Soc.*, **14**, 149—150).—Japanese menthol crystallises in small prisms, thus differing from American menthol, which forms long needles. After careful purification, American menthol melts at 42.3°, boils at 212.5° (corr.) under 742 mm. pressure, and has in the crystalline state, a sp. gr. = 0.890 at 20°/4°, and when fused, a sp. gr. = 0.8810 at 44.6°/4°. The rotatory power of menthol in alcoholic solution at 20° is expressed, for concentrations between 8 and 70 per cent. of menthol, by the equation $[\alpha] = 48.247^\circ + 0.011108q + 0.00001870q^2$, where q is the percentage of inactive solvent present. For solutions in benzene, not too dilute, the equation $[\alpha] = 49.511^\circ + 0.025634q + 0.0008403q^2 - 0.00001102q^3$ applies, whilst for solutions in acetic acid, the equation is $[\alpha] = 47.711^\circ + 0.006386q + 0.00007142q^2$. Fused menthol has the rotatory power $[\alpha]_D = -49.86^\circ$. The comparison of the physical properties of American with those of Japanese

menthol shows only very slight differences, which are probably due to a slight admixture with menthone in the former case.

A. J. G.

Amine from Dextromenthone. By A. NEGOVOROFF (*J. Russ. Chem. Soc.*, **23**, 443—446).—Dextromenthone, $[\alpha]_D = +21.6^\circ$, was prepared by Beckmann's method from menthol, m. p. 43° , and transformed into the corresponding oxime by the action of hydroxylamine and sodium hydrogen carbonate in alcoholic solution. The oxime had the specific rotation $[\alpha]_D = -9.21^\circ$. 17.5 grams, on reduction in alcoholic solution with metallic sodium, gave 7 grams of the crude amine, $C_{10}H_{19}\cdot NH_2$, about 40 per cent. of the theoretical yield. The following table exhibits the properties of this amine compared with those of the amine from lævomenthol oxime:—

	Amine from	
	Lævomenthol.	Dextromenthol.
Boiling point	206—207°	206—207° (at 747 mm.)
Sp. gr. 0°/0°	0.8685	0.8749
$[\alpha]_D$	—33.60	—9.26
Hydrochloride	long tables, rhombic	prismatic needles, rhombic
$(C_{10}H_{19}NH_2)_2H_2PtCl_6$..	golden-yellow scales	yellow silky needles

J. W.

Occurrence of Bornyl Acetate in the Ethereal Oils of *Abies sibirica* and *Abies pectinata*. By E. HIRSCHSOHN (*Chem. Centr.*, 1892, ii, 793; from *Pharm. Zeit. Russ.*, **30**, 593—595).—The author has isolated bornyl acetate from the ethereal oil of *Abies sibirica*, of which it forms 30 per cent.; this oil is therefore the best material for the preparation of borneol. The substance which Spehr obtained from oil of pine needles, and described as a terpene hydrate, is in reality bornyl acetate. The ethereal oil of *Abies pectinata* also contains bornyl acetate, which may also be assumed to be present in oil of *Pinus canadensis*.

A. J. G.

Gutta-percha. By O. OESTERLE (*Arch. Pharm.*, **230**, 641—674).—Gutta-percha was boiled with successive fresh quantities of water, until the latter was no longer coloured; by this means a tannin, sugar, and (inorganic?) salts were extracted; it was then dried, repeatedly extracted with boiling alcohol, and the alcoholic extract slowly cooled; *alban* then separated out as a white, crystalline precipitate, and the mother liquor from this, when evaporated, left a brown, resinous mass of impure *fluavil*, smelling like colophony. The residual gutta-percha was then dissolved in chloroform, the solution filtered from a small residue, and mixed with alcohol; *gutta* then separated in the form of a milky emulsion, which gradually gathered into flakes. At the same time, a stringy substance, *guttan*, was precipitated; it is, however, very unstable, for when it is

repeatedly dissolved in chloroform and precipitated with alcohol, it is gradually converted into gutta; it differs from the latter in containing oxygen.

Gutta, $(C_{10}H_{16})_n$, is a white, amorphous substance with high molecular weight, and melts at 53° . Bromine attacks it, with evolution of hydrogen bromide; it is also gradually affected by air and light, becoming yellow and friable, and partially soluble in alcohol, aqueous potash, and benzene. It is stable in the absence of light and air.

Alban, $C_{40}H_{64}O_2$, melts at 195° (uncorr.). It is attacked by bromine, with evolution of hydrogen bromide, and by nitric acid, with formation of a nitrogenous substance, but hydroxylamine and phenylhydrazine do not attack it, neither can an acetyl derivative be prepared. When distilled with phosphorus pentasulphide, it yields an oil which contains sulphur; distilled with zinc-dust, it yields liquid hydrocarbons, on which nitric acid acts, producing substances with an odour of flowers and of musk. When heated with alcoholic potash for 24 hours at 150° in a sealed tube, a hydrocarbon, *albene*, is obtained.

Fluavil, $(C_{10}H_{16}O)_n$, is a yellow, amorphous substance, melting at $82-85^\circ$; no derivative could be prepared.

The above-mentioned substances were all contained in commercial gutta-percha, and also in two samples collected exclusively from *Payena Leerii*. Of the latter, which were originally equally plastic, one had become brittle; this one was found to contain more fluavil. Gutta appears to be the essential constituent of gutta-percha, and to it the plastic properties of the latter are due. Alban is present in considerable quantity, but does not appear to materially affect these properties. Fluavil is usually present in small amount; a larger proportion of it spoils the gutta-percha, rendering it brittle and friable. All these constituents of gutta-percha are chemically inert—except that gutta (and guttan) are slowly affected by light; to this the gradual deterioration in the quality of gutta-percha when kept is doubtless to be ascribed.

C. F. B.

Brazilin Methyl Ether. By C. SCHALL (*Ber.*, 25, 3670—3672).—The author has repeated his analyses of brazilin methyl ether and of a number of bromine derivatives in order to prove whether the compound contains three or four methoxyl groups; it appears to form a tetracetyl derivative, the investigation of which is to be continued.

J. B. T.

Jalapin. By T. POLECK (*Chem. Centr.*, 1892, ii, 786—787; from *Zeit. österr. Apoth.-vereins*, 1892, 1—14).—Much of this paper consists of a recapitulation of earlier work (*Abstr.*, 1885, 669). Samelson's jalapinol (*loc. cit.*) does not exist. When jalapin is hydrolysed with hydrochloric acid, it yields dextrose and jalapinolic acid, which has the formula $C_{16}H_{30}O_3$ (not $C_{16}H_{30}O_4$, as previously stated). It is odourless, crystallises in tufts of white needles, and melts at $63-64^\circ$. The formula was confirmed by analyses of the silver, barium, and ethyl salts.

A. J. G.

Names of New Remedies. By J. D. RIEDEL (*Chem. Centr.*, 1892, ii, 584—586; from *Apoth.-Zeit.*, 7, 405—406).—A list of the

names under which various organic chemicals have been recently introduced as drugs.

Opium Smoke. By H. MOISSAN (*Compt. rend.*, **115**, 988—992).—The opium specially prepared for smoking, or *chandoo*, is dried immediately before use, at a temperature that does not exceed 240° , and is smoked at a temperature of about 250° . Combustion of *chandoo* in a current of air at 250° produces only a small quantity of fragrant oils, and a small quantity of morphine, which is probably carried forward by the water vapour.

The *dross*, or residue left when *chandoo* is smoked in this way, is used, together with more or less adulterated opium, by the less wealthy smokers. Combustion of the *dross* and the adulterated opium requires a temperature not lower than 300° , and in this case the decomposition is more complicated, and the volatile products contain pyrroline, acetone, and hydropyridic and pyridic bases (compare next abstract and this vol., ii, 179). C. H. B.

Tobacco Smoke. By A. GAUTIER (*Compt. rend.*, **115**, 992—993).—Researches, which will shortly be described in detail, show that when tobacco is smoked in a pipe, the volatile liquid products chiefly consist of basic compounds. They contain a large proportion of nicotine, a higher homologue of nicotine, $C_{11}H_{16}N_2$, which pre-exists in tobacco leaves, and a base, C_6H_7NO , which seems to be a hydrate of picoline. Other less volatile bases, including hydropyridines, are also formed. These alkaloids result from the decomposition, at a comparatively low temperature, of the carbopyridic and carbohydropyridic or analogous acids present in the tobacco. C. H. B.

Constitutions of the Methylpyrrolines. By C. U. ZANETTI (*Gazzetta*, **22**, ii, 269—276).—The methylpyrroline boiling at 148 — 150° yields, with hydroxylamine hydrochloride, a dioxime, $C_5H_8(NO)_2$, which crystallises in lustrous, white scales melting at 73 — 74° ; it is very soluble in all the ordinary solvents, with the exception of light petroleum. Inasmuch as it gives a ketonic acid on treatment with potash, it is most probably the dioxime of levulinic aldehyde, and the pyrroline from which it is derived must be α -methylpyrroline (compare Zanetti, *Abstr.*, 1892, 74).

The methylpyrroline which boils at 142 — 143° , obtained by Dennstedt's method (*Abstr.*, 1891, 1501), when treated with hydroxylamine hydrochloride, yields the dioxime melting at 73 — 74° , and a small quantity of a substance melting at 159 — 160° . The latter is probably derived from β -methylpyrroline, but owing to the small quantity of it obtained, no analysis could be made. W. J. P.

Action of Propyl Alcohol on Pyrroline. By M. DENNSTEDT (*Ber.*, **25**, 3636—3637).—When a mixture of propyl alcohol and pyrroline is distilled over heated zinc-dust, a product is obtained which may be divided, by fractional distillation, into five fractions.

Fraction 1, boiling at 173 — 175° , has the properties and composition of a *c*-propylpyrroline, C_7NH_{11} , and is a bright oil, which quickly turns

yellow on exposure to light. The acetyl compound, obtained by the action of acetic anhydride, boils at 270° . The *c*-propylcinnamylpyrroline, obtained by the action of benzaldehyde, crystallises in yellow needles, and melts at $148\text{--}150^{\circ}$, whilst the *n*-acetylpropylpyrroline is a dark yellow, viscid oil, and boils at 245° . When an ethereal solution of the propylpyrroline is treated with dry hydrogen chloride, dipropyldipyrroline hydrochloride is obtained; and on treating this salt with sulphuric acid, it is converted into dipropylindole. The latter boils at 305° , and gives a picrate melting at $98\text{--}100^{\circ}$.

Fraction 2 boils at $185\text{--}187^{\circ}$, and has also the properties and composition of a *c*-propylpyrroline. The *c*-acetyl compound boils at 275° . The *n*-acetyl compound boils at 250° . The propylcinnamylpyrroline crystallises from alcohol in lustrous cubes, and melts at $161\text{--}162^{\circ}$. The dipropylindole boils at 290° .

Fraction 3 boils at $205\text{--}210^{\circ}$, and is a *c*-dipropylpyrroline. The *c*-acetyl compound boils at $270\text{--}280^{\circ}$, the *n*-acetyl compound at $250\text{--}260^{\circ}$.

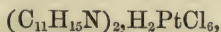
The last two fractions, boiling at $270\text{--}280^{\circ}$ and $300\text{--}310^{\circ}$, are isomerides of the mesitylpyrroline and phoronpyrroline obtained from acetonepyrroline.

E. C. R.

Trimethyltetrahydroquinoline. By A. FERRATINI (*Gazzetta*, **22**, ii, 417—422; compare *Abstr.*, 1892, 614).—Trimethyldihydroquinoline is readily reduced by tin and hydriodic acid, with production of trimethyltetrahydroquinoline; the *hydriodide* of the latter, $\text{C}_9\text{H}_9\text{Me}_3\text{HI}$, forms small, white prisms, which melt at 197° . The methiodide, when distilled with potash, merely loses methyl iodide, giving the free base. On heating trimethyltetrahydroquinoline with hydriodic acid and red phosphorus in closed tubes at 250° , methyl iodide is obtained, together with a base which seems to be *dimethyltetrahydroquinoline*, $\text{C}_9\text{H}_9\text{Me}_2$, as it gives a *nitronitrosamine*, $\text{C}_{11}\text{H}_{13}\text{N}(\text{NO})\cdot\text{NO}_2$, with nitrous acid. This substance crystallises in large, thin, transparent, yellow plates, melts at $154\text{--}155^{\circ}$ with slight decomposition, and gives Liebermann's reaction.

W. J. P.

Tetrahydroisoquinoline. By A. FERRATINI (*Gazzetta*, **22**, ii, 422—430; compare preceding abstract).—Tetrahydroisoquinoline reacts energetically with methyl iodide, yielding a mixture of methyltetrahydroisoquinoline hydriodide and *methiodide*, $\text{C}_{10}\text{H}_{13}\text{N}\cdot\text{MeI}$; the latter forms white scales, melts at 189° , and turns yellow on exposure to the air. On treating it with silver chloride suspended in water, a solution is obtained which yields an *aurochloride* of the composition $\text{C}_{11}\text{H}_{15}\text{N}\cdot\text{HAuCl}_4$; this forms lustrous, yellow laminae, and melts at $184\text{--}185^{\circ}$; the corresponding *platinochloride*,



forms beautiful, yellow needles melting at 228° with decomposition.

On heating methyltetrahydroisoquinoline methiodide with potash, a base distils, which, when suitably purified, combines with methyl iodide with development of heat, forming a *methiodide* of the composition $\text{C}_{12}\text{H}_{18}\text{NI}$. This is obtained in long, rectangular plates melt-

ing with decomposition at 200—201°; on distillation with potash, it yields a base, which gives a yellow, crystalline *aurochloride* melting at 105°.

W. J. P.

Synthesis of Isoquinoline Derivatives. By S. GABRIEL and A. NEUMANN (*Ber.*, **25**, 3563—3573; compare *Abstr.*, 1887, 1112).—*Diacetylorthocyanobenzyl cyanide*, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{Ac})_2\cdot\text{CN}$, forms small, lustrous needles, melts at 137—138°, and when heated with 75 per cent. acetic acid saturated with hydrogen chloride, yields 3'-methylisocoumarin (*isobenzalphthalide*), $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{CH:CMe} \\ \text{CO}\cdot\text{O} \end{smallmatrix}$, melting at 73—74°, and isomeric with ethylidenephthalide (*Abstr.*, 1886, 243). On heating the compound with alcoholic ammonia, 3'-methylisocarbostyryl, $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{CH:CMe} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$, is formed; this crystallises from alcohol in rectangular prisms, and melts at 211°. 3':4'-Methylcyanisocarbostyryl, obtained by dissolving diacetylorthocyanobenzyl cyanide in warm, dilute alkali hydroxides, forms minute, white needles, melts above 310°, is insoluble in ordinary solvents and ammonia, and gives 3'-methylisocarbostyryl on being heated with dilute sulphuric acid. 2':3':4'-Dimethylcyanisocarbostyryl is obtained by methylating 3':4'-methylcyanisocarbostyryl; it crystallises in delicate needles, melts at 182—183°, and, when heated with dilute sulphuric acid, yields 2':3'-dimethylisocarbostyryl, which crystallises in colourless prisms, melts at 103°, and decomposes into 3'-methylisocoumarin and methylamine on being heated at 230° with hydrochloric acid in a sealed tube. 1':3'-Chloromethylisoquinoline is produced by boiling 3'-methylisocarbostyryl with phosphorus oxychloride; it is volatile with steam, melts at 35—36°, boils at 280—281° (757 mm.), and when heated in a sealed tube with hydriodic acid and phosphorus, furnishes 3'-methylisoquinoline. The latter melts at 68°, boils at 246° (761 mm.), and is volatile with steam; the *platinochloride* melts at 195°, and the *picrate* at 197—198°. When a mixture of 3'-methylisocarbostyryl and zinc-dust is heated to a dull red heat in a current of hydrogen, 3'-methylisoquinoline distils over.

3':4'-Phenylcyanisocoumarin, $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{C(CN):CPh} \\ \text{CO} \text{---} \text{O} \end{smallmatrix}$, is obtained by heating orthocyanobenzyl cyanide with benzoic chloride; it forms a citron-yellow, microcrystalline powder, melts at 204—205°, is sparingly soluble in hot alcohol, and yields isobenzalphthalide (*Abstr.*, 1885, 1231) when heated at 180° with 75 per cent. acetic acid saturated with hydrogen chloride, and 3':4'-phenylcyanisocarbostyryl, when heated at 180° with alcoholic ammonia; the latter crystallises in lemon-yellow needles, melts at 270°, and is sparingly soluble in alcohol. 3'-Phenylisoquinoline is more easily prepared by distilling a mixture of 3'-phenylisocarbostyryl and zinc-dust in a current of hydrogen than by the method formerly given (*Abstr.*, 1886, 226).

A. R. L.

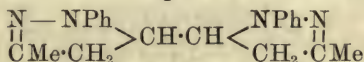
Preparation and Properties of Methyloxythiazole. By J. TCHERNIAC (*Ber.*, **25**, 3648—3652).—Methyloxythiazole is readily

prepared by the action of sodium hydrogen carbonate on thiocyanacetone in aqueous solution at the ordinary temperature; the clear liquid, after separation from resinous products, is repeatedly extracted with boiling ether in an apparatus devised by the author, a sketch of which is given in the original paper. The yield is 41.6 per cent. of the theoretical. The thiazole crystallises in pale, cream-coloured needles or prisms melting at 105—106°, and solidifying at 97—98°. A molecular weight determination by Raoult's method proves that the substance has the simple formula C_4H_5SNO . J. B. T.

The Pyrazoline Reaction. By L. KNORR (*Ber.*, **26**, 100—103).—Pyrazoline bases derived from phenylhydrazine, when treated with oxidising agents in acid solution, are converted into magenta-red to blue dyes, and by this reaction very small quantities of pyrazolines can be detected. The reaction is equally applicable to pyrazoles derived from phenylhydrazine, if they are first reduced with sodium and alcohol to the corresponding pyrazoline.

This reaction is applicable to pyrazoles derived from phenylhydrazine which do not contain oxygen, and also to derivatives of 1-phenylpyrazole. Pyrazolones derived from phenylhydrazine do not, as a rule, give this reaction, but 1-phenyl-3:4-trimethylpyrazolone is an exception. The pyrazolones obtained from hydrazine hydrate do not give the reaction, even if they contain a benzene residue substituted in the pyrazole nucleus. Thus pyrazole and its homologues, phenylmethylpyrazole (from benzoylacetone and hydrazine hydrate), and 3:5-diphenylpyrazole (from dibenzoylmethane and hydrazine) do not give the reaction. The reaction seems to be determined by the presence of a benzene residue in the position 1.

The author has obtained a compound of the formula



by the careful oxidation both of 1-phenyl-3-methylpyrazoline and of 1:5-diphenyl-3-methylpyrazoline. In the case of the latter compound, the condensation takes place with elimination of the 5-phenyl group. It crystallises from acetic acid in characteristic silvery leaflets, melts at 275—278°, and dissolves in mineral acids with a magenta coloration. E. C. R.

Pyrazole Derivatives from Unsaturated Acids and Hydrazines. By L. KNORR and P. DUDEN (*Ber.*, **26**, 103—108, 109—111).—The authors have already described (*Abstr.*, 1892, 731) 1:3:5-phenylmethylpyrazolidone. The 2-acetyl derivative crystallises in needles easily soluble in boiling water, alcohol, glacial acetic acid, and ether, and melts at 126°. The 2-benzoyl derivative crystallises in plates insoluble in water, and melts at 162°. The 2-nitroso-derivative forms pale-yellow needles melting at 54—55°, and is very unstable, being readily reconverted into the pyrazolidone by reducing agents. A methiodide of the pyrazolidone was also obtained; it decomposes at 310° without previous fusion.

The pyrazolidone is easily reduced by the action of sodium and

alcohol, phenylmethylpyrazolidine and *phenylmethylpyrazoline* being formed. The latter is a feeble base, its salts being decomposed by water, and is volatile in steam; it is not oxidised by mercuric oxide, or by Fehling's solution. It melts at 72—74°, and boils at 289° under 757 mm. pressure. The authors also prepared it by the reduction of 1 : 3-phenylmethylpyrazole.

In order, if possible, to determine whether the space configuration of the unsaturated acids influences their condensation with hydrazines, the action of the liquid isocrotonic acid on phenylhydrazine was studied. The same pyrazolidone of m. p. 84° was obtained as from the solid acid, although the yield was much less. As, however, J. A. Wislicenus has now shown (*Inaug. Dissert.*, Leipzig, 1892) that the liquid acid is probably a molecular mixture of the two geometrically isomeric modifications, the results obtained leave the point in question unsettled.

The authors have further investigated the compound $C_{15}H_{12}N_2O$, previously obtained by Knorr by the distillation of the hydrazide of cinnamic anhydride (Abstr., 1887, 665). By treatment with phosphorus pentasulphide, it is reduced to 1 : 5-diphenylpyrazole (see next abstract) of m. p. 55°, and is therefore 1 : 5 : 3-diphenylpyrazolone,

$$NPh < \begin{array}{c} NH \cdot CO \\ | \\ CPh \cdot CH \end{array}$$
 When heated with excess of methyl iodide, it

yields 1 : 5 : 2 : 3-diphenylmethylpyrazolone; this is sparingly soluble in cold, but easily in boiling water, also in alcohol and in chloroform. It crystallises in scales melting at 139°, and is more basic than diphenylpyrazolone; its *picrate* forms needles melting at 180—181°. A solution of the base in strong sulphuric acid is coloured cherry-red by the addition of a drop of potassium dichromate solution.

L. T. T.

Isomerism of the Diphenylpyrazoles and of the Pyrazole Derivatives from Ethyl Benzoylacetoacetate and Ethyl Benzalacetoacetate. By L. KNORR and P. DUDEN (*Ber.*, 26, 111—116).—The authors have re-examined the various diphenylpyrazoles to establish their constitution and to reconcile the various conflicting statements concerning them.

1 : 5-Diphenylpyrazole melts at 55° and boils at 337° under 736 mm. pressure. It is the pyrazole which has been obtained (1) from cinnamic acid (see preceding abstract), (2) from benzoylpyruvic acid (Beyer and Claisen, Abstr., 1887, 943), (3) from benzoylaldehyde (Claisen and Fischer, Abstr., 1888, 690), (4) from diphenylpyrazole-dicarboxylic acid (Knorr and Laubmann, Abstr., 1889, 409), and (5) from ethyl phenylacetoacetate (Bischler, this vol., i, 44). The corresponding 1 : 5-diphenylpyrazoline melts at 136—137°.

1 : 3-Diphenylpyrazole melts at 84°, boils at 341—342° under 270 mm. pressure, and forms glistening, white crystals. It has been obtained by the authors from ethyl benzoylacetoacetate, from 1 : 3-diphenylpyrazole-4 : 5-dicarboxylic acid (from ethyl benzalacetoacetate) and from benzoylaldehyde. Whilst Claisen and Fischer obtained from benzoylaldehyde the pyrazole melting at 55°, the authors only obtained that melting at 84°. Apparently slight modifications of the conditions of experiment cause a difference in the direction of the

reaction. The corresponding 1 : 3-diphenylpyrazoline melts at 104°, but not sharply.

3 : 5-Diphenylpyrazole melts at 200° and boils at 347° under 155 mm. pressure, is crystalline, and does not form a pyrazoline. The authors have prepared this pyrazole from dibenzoylmethane.

1 : 3-Diphenylpyrazole-4 : 5-dicarboxylic acid,
$$\text{N} \begin{array}{c} \text{NPh} \cdot \text{C} \cdot \text{COOH} \\ \parallel \\ \text{CPh} \cdot \text{C} \cdot \text{COOH} \end{array}$$
 was obtained by the oxidation of diphenylmethylpyrazolecarboxylic acid; it melts at 190°. Its *barium salt* crystallises in needles. At 200—250°, the acid gives off carbonic anhydride, and yields 1 : 3-diphenylpyrazole. L. T. T.

Pyrazoles from Unsaturated Acids and Hydrazines. By P. DUDEN (*Ber.*, 26, 117—122).—The author has extended his previous work to bibasic unsaturated acids containing, or probably containing, the group $-\text{CH}:\text{CH}\cdot\text{COOH}$. Both maleïc and fumaric acids, when heated at 110° with one equivalent of phenylhydrazine, yielded

1 : 5 : 3-phenylpyrazolidonecarboxylic acid,
$$\text{NPh} \begin{array}{c} \text{NH} \cdot \text{CH} \cdot \text{COOH} \\ \parallel \\ \text{CO} \cdot \text{CH}_2 \end{array}$$
,

which is sparingly soluble in cold water, crystallises in concentrically grouped needles, and melts with partial decomposition at 201—202°. Its *sodium salt* is amorphous and deliquescent; its *silver salt* forms a white precipitate, which deposits silver when boiled with water. The acid reduces Fehling's solution, mercuric oxide, ferric chloride, &c. By careful oxidation with ferric chloride, it yields 1 : 5-phenylpyrazolidonecarboxylic acid, melting at 265°, and described by W. Wislicenus (*Ber.*, 1887, 234). In glacial acetic acid solution, the formation of a pyrazolidone does not take place, fumaric acid remaining unchanged, and maleïc acid yielding maleïlphenylhydrazine (Hotte, *Abstr.*, 1887, 671). When fumaric or maleïc acid is heated with excess (three equivalents) of phenylhydrazine, *phenylhydrazinesuccinyl-dihydrazide*, $\text{N}_2\text{H}_2\text{Ph} \cdot \text{C}_2\text{H}_3(\text{CO} \cdot \text{N}_2\text{H}_2\text{Ph})_2$, is formed. This substance is insoluble in water and ether, and but sparingly soluble even in boiling alcohol; it crystallises in needles, and melts at 199—200°. Strong alkalis or acids resolve it into 1 : 5 : 3-phenylpyrazolidonecarboxylic acid and phenylhydrazine.

Oleïc acid yields a *hydrazide*, $\text{C}_{24}\text{H}_{40}\text{N}_2\text{O}$, which forms crystals melting at 72—73°, and elaidic acid a *hydrazide*, $\text{C}_{24}\text{H}_{40}\text{N}_2\text{O}$, which crystallises in needles melting at 98—99°, but from neither acid could a pyrazole derivative be obtained. The author considers it probable, therefore, that neither of these acids contains the group $-\text{CH}:\text{CH}\cdot\text{COOH}$. L. T. T.

Action of Hydriodic acid on Cinchonidine. By G. NEUMANN (*Monatsh.*, 13, 651—662; compare Skraup, *Abstr.*, 1892, 83).—*Trihydriodocinchonidine*, $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O} \cdot 3\text{HI}$, is obtained by heating cinchonidine with five times its weight of hydriodic acid (sp. gr. 1.7) for $2\frac{1}{2}$ hours. It crystallises in yellowish-white needles, which become transparent at 140°, and melt, with decomposition, at 216°. When decomposed with 1 and 2 mol. proportions respectively of alcoholic ammonia, it gives rise to the compounds $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O} \cdot 2\text{HI}$ and

$C_{19}H_{22}N_2O, HI$. Of these, the former is pale yellow, melts at 184° , and decomposes with evolution of gas at 221° ; the latter melts at 166° , forms a sulphate, $C_{19}H_{22}N_2O, HI, H_2SO_4$, and when boiled with alcoholic potash yields β -cinchonidine, $C_{19}H_{22}N_2O$.

β -Cinchonidine crystallises from alcohol in plates, melts at 244° , and gives the following salts:—The *oxalate*, $C_{19}H_{22}N_2O, H_2C_2O_4$, crystallises in colourless needles, which melt at 118° and decompose at 151° ; the *tartrate*, $C_{19}H_{22}N_2O, C_4H_6O_6$, melts with decomposition at 218° ; and the two *platinochlorides*, $C_{19}H_{22}N_2O, H_2PtCl_6$ and $2C_{19}H_{22}N_2O, H_2PtCl_6$. On heating with hydriodic acid, β -cinchonidine gives the above-described trihydriodocinchonidine, melting at 216° . The latter is converted by silver nitrate into γ -cinchonidine, which melts at 238° , does not give such characteristic salts as β -cinchonidine, and forms the two platinochlorides $C_{19}H_{22}N_2O, H_2PtCl_6$ and $2C_{19}H_{22}N_2O, H_2PtCl_6$. On distillation with water, trihydriodocinchonidine yields a product which has the aldehydic property of reducing ammoniacal silver nitrate.

G. T. M.

Sparteïne. By F. B. AHRENS (*Ber.*, **25**, 3607—3612).—An aqueous solution of oxysparteïne (Abstr., 1891, 842) reduces Fehling's solution on being warmed with it. The *hydrochloride* crystallises with 1 mol. H_2O , and melts above 230° ; from more dilute solutions, however, it separates with 4 mols. H_2O ; the crystals are completely dehydrated at 160° , not, however, without partial decomposition. The *hydrobromide* crystallises with $3\frac{1}{2}$ mols. and with $2\frac{1}{2}$ mols. H_2O , and the *hydriodide* crystallises with 1 mol. H_2O . The *nitrate* forms large, transparent tables (with 1 mol. H_2O), sinters at 202° , and melts at 207° . The *methiodide*, $C_{15}H_{24}N_2O, MeI$, crystallises in yellowish needles, and melts at 191 — 193° ; on adding freshly precipitated silver chloride to its aqueous solution, the *methochloride* is obtained. The latter yields a *platinochloride*, $C_{15}H_{24}N_2O, HMePtCl_6 + H_2O$, which forms transparent red crystals, and melts at 228 — 229° , and an *aurochloride* melting at 190 — 191° . Oxysparteïne is not attacked when heated at 250° with concentrated sulphuric acid, or when warmed with nitric acid; hydroxylamine and phenylhydrazine are without action on it. When heated at 150° with phosphorus oxychloride, it is converted into an oily base, which yields an *aurochloride*, $C_{15}H_{22}N_2, 2HAuCl_4$, crystallising in needles, and melting at 160 — 161° . Hürthle finds that oxysparteïne strengthens the heart's action (see also *Arch. experim. Pathol. Pharm.*, 1892, 141).

Dioxysparteïne, $C_{15}H_{26}N_2O_2$ (Abstr., 1887, 1056), is the ultimate product of the action of hydrogen peroxide on sparteïne. The *hydrobromide* forms colourless crystals, and melts at 146 — 147° , whilst the *hydriodide* melts at 137° . The free base prepared from these salts crystallises in translucent prisms, and melts at 128 — 129° . The *mercurochloride* melts at 193° .

Trioxysparteïne is obtained by the action of hydrogen peroxide on oxysparteïne; it is crystalline, but has not been prepared quite pure. The *platinochloride*, $(C_{15}H_{24}N_2O_3)_2, H_2PtCl_6 + 3\frac{1}{2}H_2O$, crystallises in orange needles, and decomposes at about 200° ; the *aurochloride* forms long, lance-shaped crystals, and melts at 136 — 137° . The research is proceeding.

A. R. L.

Behaviour of Hydrochloric acid to Albumin in relation to the Chemical Investigation of Gastric Juice. By L. SANSONI (*Chem. Centr.*, 1892, ii, 876—875; from *Berlin klin. Woch.*, 29, 1043—1045, 1084—1089).—An aqueous solution of albumin has the property of uniting with a certain quantity of hydrochloric acid, so that the acidity of the mixed solution is diminished, and the more concentrated the albumin solution the more acid is thus concealed. This loss can be shown either by the phloroglucinol-vanillin method, or by the employment of phenolphthaleïn. With peptone, it is only in the case of the first of the reagents that part of the acid is not recognisable, and the complete peptonisation of albumin seems to set free any hydrochloric acid previously retained by it; in the intermediate stages of the peptonisation, the loss of acidity is proportional (inversely?) to the duration of the artificial digestion, and, therefore, to the amount of albumin converted into peptone. A mixture of albumin and hydrochloric acid does not recover the lost acidity when kept for a long time at 38°, even if pepsin is present, provided the conditions are so arranged that much peptonisation does not occur. By the continued action of a temperature of 100—110°, the acidity is partly or wholly lost, but this does not occur with mixtures of peptone with hydrochloric acid.

This combination of albumin with hydrochloric acid does not seem to take place in constant proportion; where the mixture has not been heated to higher temperatures, the greater portion of the hydrochloric acid can be removed by dialysis.

The behaviour at 100—110°, described above, leads to the conclusion that all methods for the estimation of free hydrochloric acid in gastric juice, depending on the evaporation of the gastric juice, must be erroneous, inasmuch as too little free hydrochloric acid will be found.

A. J. G.

Albumoses and Peptone. By W. KÜHNE (*Zeit. Biol.*, 29, 1—40).—Solutions containing a mixture of albumoses and peptone give a precipitate of albumoses when saturated with ammonium sulphate, the peptone remaining in solution. After filtration, the filtrate, if set aside, will subsequently give a further precipitate if more salt is added. This has been explained by supposing that the saturation was in the first instance incomplete, or that the peptone is partially changed back into albumose. The present research shows that the former is the more probable explanation. There are many precautions necessary, in order to precipitate the last traces of albumose. It is necessary in the first instance to use large volumes of the saturated solution in addition to merely adding crystals of the salt to the proteïd mixture. Further, it is found that whereas the greater part of the albumose is precipitated by the salt if the reaction of the mixture is made acid, the residue which is difficult of precipitation comes down more readily if the reaction is made alkaline. It is further necessary after the solution of peptone is obtained to remove the salt employed; a method for doing this by the use of barium carbonate after concentration is fully described. If pancreatic juice has been used for the preparation of peptone, care also must be taken that leucine and tyrosine are removed also. In drying, concen-

trating, &c., especially if sulphuric acid is used, a brownish product is formed; this is minimised by care in the manipulations. This substance is precipitable by ammonium sulphate, it is not, however, albumose; it gives no biuret reaction. Further, if a precipitate forms in dialysis, it is not necessarily of proteid nature; if hard water is used, it may be calcium sulphate.

Pekelharing does not seem to have noticed the necessity of these and other precautions and details, and much of the present paper is polemical, showing Pekelharing's supposed errors, and pointing out that there are more differences between peptones and albumoses than a mere difference of solubility in ammonium sulphate.

Diffusibility of Albumoses and Peptone.—Hetero-albumose is the least diffusible of the albumoses; in neutral saline solutions it is precipitated, and there is no loss in dialysis. Dissolved in ammonia it loses 5.22 per cent. Deutero-albumose comes next (loss 24.1 per cent.); then proto-albumose (loss 28.3 per cent.). Peptone loses 51 to 51.8 per cent.

Koch's tuberculin contains an indole-like substance in addition to albumoses (small quantities of proto-albumose, large quantities of deutero-albumose). In the process of the action of the tubercle bacillus, proto-albumose is first formed, then deutero-albumose. The bacteria so far act like digestive ferments, but there is little or no true peptone formed, and leucine and tyrosine are also absent. Tuberculin also gives a colour with bromine; this substance, tryptophan or proteïnchromogen, is probably a mixture of the indole-like substance with other not fully recognised materials.

The hay bacillus acts somewhat differently when grown in solutions of proto-albumose, for not only are secondary albumoses formed, but also true peptone, tyrosine, leucine, tryptophan, and ammonia. It is thus very like trypsin in its action.

With *Bacillus prodigiosus* very little albumose remains; it is almost entirely broken up into peptone, leucine, tyrosine, tryptophan, and the indole yielding substance.

In no case was there any formation of hydrogen sulphide.

W. D. H.

Certain Chemical Constituents of the Medulla of Nerve.

By A. KOSSEL and F. FREYTAG (*Zeit. physiol. Chem.*, **17**, 431—456).—Attention is in the present research directed to the cerebrosides, constituents, apparently, of the medullary sheath of nerve fibres, not of the axis cylinders.

The substance called protagon is not a single material, but there is more than one protagon. They yield either one of two, or, perhaps, three, derivatives called cerebrin, kersin or homocerebrin, and encephalin; and further, probably several lecithins are obtainable from the different protagons. The protagons resemble each other in the following points:—

1. They contain C, H, N, O, P, and, in part, S.
2. By oxidation with nitric acid, they yield higher fatty acids.
3. By the action of boiling sulphuric or hydrochloric acid, reducing carbohydrates are formed.
4. By the action of alkalis they yield cerebrosides, which further

split into ammonia, galactose, and a third complex material, which, on fusion with potash, yields higher fatty acids.

Elementary analysis of protagon crystals, prepared as Gamgee and Blankenhorn direct (*Zeit. physiol. Chem.*, **3**, 260), gave practically the same results as in their and Baumstark's (Abstr., 1885, 918) analyses. The pure crystals yield the two cerebrosides cerebrin and kersin among their decomposition products. The analyses of these substances agree well with those of Thudichum, Parcus, and others. Their molecular weight was investigated by Beckmann's boiling method and by the analysis of their barium and bromine compounds. They further yield, by treatment with nitric acid, a fatty acid, recognised as neurostearic acid by Thudichum, and correctly analysed but not identified by Müller. It is, in fact, stearic acid, 3 mols. of which are formed from cerebrin for every 2 atoms of nitrogen. From all these considerations the formula given to cerebrin is $C_{70}H_{140}N_2O_{13}$, and to kersin $C_{70}H_{138}N_2O_{12}$.

Similar substances have been described in other parts of the body; in the present investigation two were separated from pus; these are designated pyosin, $C_{87}H_{110}N_2O_{15}$, or $C_{58}H_{110}N_2O_{15}$, and pyogenin, $C_{65}H_{128}N_2O_{19}$.

The opinion is expressed that these substances and the similar ones in testicular cells are contained in the cytoplasm, not in the nucleus.

W. D. H.

Chemical Constitution of Peptones. By P. SCHÜTZENBERGER (*Compt. rend.*, **115**, 764—768).—Fibrin-peptone, obtained from the blood of the horse in the manner previously described, is evidently not homogeneous. If a somewhat syrupy solution obtained by concentration on a water-bath is mixed with gradually increasing quantities of strong alcohol, precipitates are obtained which are more and more soluble in alcohol. About one-fifth of the fibrin-peptone remains in solution, even when the liquid contains from 85 to 90 per cent. of alcohol. The composition of the various fractions is not identical, but indicates that they are probably different terms in a homologous series. The first precipitate has the composition $C_{29}H_{51}N_8O_{13}$, whilst the mean composition of all the fractions is $C_{31}H_{55}N_8O_{13}$. The portion soluble in alcohol has the composition $C_{30}H_{56}N_8O_{13}$. The various fractions, when heated for four or five hours at 180° with 3 parts of barium hydroxide, all behave like fibrin-peptone and yield ammonia, carbonic anhydride, acetic acid, and a non-volatile residue consisting of a mixture of amido-acids. This residue, in all cases, when dried in a vacuum at the ordinary temperature, has the composition $mC_9H_{18}N_2O_5$; if heated at 100° , it loses water. The similar residue obtained from the fraction soluble in alcohol has the composition $mC_9H_{20}N_2O_5$.

Phosphotungstic acid, free from alkalis, precipitates only about half the fibrin-peptone. The precipitated fraction, when separated from the phosphotungstic acid and dried in a vacuum over sulphuric acid, is a colourless, friable substance, soluble in water but not hygroscopic. It contains oxygen and nitrogen in the ratio of 1.27 : 1, and carbon and hydrogen in the ratio of about 1 : 1.9. When heated with barium hydroxide, it loses about one-fourth of its nitrogen in the form of ammonia and 1 mol. of carbonic anhydride is liberated for

every 2 mols. of ammonia. The residue of amido-acids has the composition $p(C_nH_{2n}N_2O_4)$ or $C_nH_{2n}NO_2$, n being between 9 and 10 and very near 9.

The portion not precipitated by phosphotungstic acid contains oxygen and nitrogen in the ratio of 2:1, and carbon and hydrogen in the ratio of 1:1.7. When heated with barium hydroxide, it loses one-fifth of its nitrogen in the form of ammonia. 1 mol. of carbonic anhydride is formed for every 2 mols. of ammonia, and the other products are acetic acid and a residue of amido-acids of the composition $p(C_nH_{2n}N_2O_6)$ where n is again between 9 and 10 and is very near 9.

The portion of the fibrin-peptone soluble in alcohol gives similar results except that it contains C_nH_{2n+2} instead of C_nH_{2n} .

It follows that fibrin-peptone from the horse can be split up into two parts by the action of phosphotungstic acid, one which is precipitated and contains a lower proportion of oxygen, and another which is not precipitated and contains a higher proportion of oxygen. The excess of oxygen in the latter exists in the form of hydroxyl, and the fibrin itself must be regarded as a compound ether hydrolysable by pepsin, yielding two products which are both ureides.

C. H. B.

γ -Achroglobin, a New Respiratory Globulin. By A. B. GRIFFITHS (*Compt. rend.*, 115, 738—739).—The blood of the *Tunicata* (*Ascidia*, *Molgula*, *Cynthia*) contains a third achroglobin which, like those obtained from *Patella* and the *Chitons*, dissolves in alkaline carbonates and phosphates. It has the composition $C_{721}H_{915}N_{194}SO_{1837}$ and exists in two states, oxidised and reduced, and may be called γ -achroglobin. 100 grams absorb 149 c.c. of oxygen at 0° and 760 mm. It loses its oxygen in a vacuum and the reduced γ -achroglobin combines with methane, carbonic oxide, and acetylene, forming colourless compounds which dissociate in a vacuum. When dissolved in a solution of magnesium sulphate, its specific rotatory power is $[\alpha]_D = -63^\circ$.

It is highly probable that several colourless respiratory substances exist in the blood of invertebrates.

C. H. B.

Pigments of Lepidoptera. By A. B. GRIFFITHS (*Compt. rend.*, 115, 958—959; compare Hopkins, *Proc.*, 1889, 117).—A green pigment is obtained from the wings of butterflies of several genera and species by extracting them with dilute acid, after cleaning them with alcohol and ether. On evaporating the clear extract, the pigment separates.

Lepidopterac acid, $C_{11}H_{12}N_8O_{10}$, is bibasic, dissolves in alkalis, and forms a *disilver salt*, of which the rotatory power in alcoholic solution is $[\alpha]_D = +29^\circ$. By prolonged boiling with water, the acid is split up into carbamide, alloxan, and carbonic anhydride, but on similar treatment with hydrochloric acid, it is converted into carbonic anhydride and uric acid. It is thus probably a derivative of the latter, deposited in the wings by wandering cells, and therefore of excretory nature.

JN. W.

Organic Chemistry.

Californian Petroleum. By F. LENGFELD and E. O'NEILL (*Amer. Chem. J.*, **15**, 19—21).—The crude petroleum from Pico Cañon, in the San Fernando Mountains, Los Angeles County, is viscid, and of a dark-green colour. Its sp. gr. is 0·8414 at 15°, and its refractive index is 1·4810 at 14°. When fractionated, it yields oils boiling from below 40° to 300°, and having sp. gr. varying from 0·6344 to 0·8649, and refractive indices varying from 1·3669 to 1·4824. The lower fractions are colourless; the higher are slightly coloured, and have a marked fluorescence. A preliminary examination shows that the oil contains paraffins, naphthenes, and homologues of benzene, and is probably intermediate in character between Pennsylvanian and Russian petroleum. JN. W.

Some Cases of Isomerism in the C₆ Series. By G. GRINER (*Ann. Chim. Phys.* [6], **26**, 305—394).—The author has studied the tetrabromides and dihydriodides of diallyl, and has prepared a number of new unsaturated fatty hydrocarbons and their derivatives; most of the compounds investigated were found to exist in two or more geometrically isomeric forms, the number of which frequently equalled, but in no case exceeded, that of the modifications foreseen by the theory of Le Bel and Van't Hoff. The first part of the paper is devoted to a discussion of the geometrical constitution of the compounds in question.

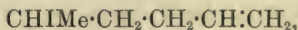
Diallyl is best prepared by adding allyl iodide (5 parts) in small quantities at a time to a finely divided alloy (6 parts) of tin (4 parts) and sodium (1 part), heated at about 110°; the product is purified by fractional distillation, the yield being more than 95 per cent. of the theoretical.

When diallyl, boiling at 58·5—59·5°, is treated with bromine in chloroform solution at a temperature below -10°, it yields the two tetrabromides, C₆H₁₀Br₄, described by Sabanéeff. The one melts at 53—54°, and crystallises in plates which seem to belong to the clinorhombic system, whilst the other melts at 64—65°, and crystallises in orthorhombic prisms; the liquid tetrabromide described by Ciamician and Anderlini is not formed under the conditions employed by the author. The formation of two dibromides from diallyl is in accordance with stereochemical considerations, and is not to be ascribed to the presence of dipropenyl (compare Wagner, *Abstr.*, 1889, 226; 1890, 223), the tetrabromides of which have properties quite different from those of either of the compounds obtained from diallyl; as, moreover, dipropenyl boils above 77°, whereas diallyl boils at 58·5—59·5°, the presence of the former in the preparations employed by the author is highly improbable.

Two stereoisomeric *dihydriododiallyls*, CHMeI·CH₂·CH₂·CHMeI, are formed, together with the monhydrido-compound boiling at

57—58°, under a pressure of 10 mm., described by Wurtz, when anhydrous hydrogen iodide is passed into diallyl cooled to -20° ; the one is a crystalline substance melting at 44° , and boiling at $133-134^{\circ}$, under a pressure of 15 mm.; the other does not solidify even at -60° , and boils at $132-133^{\circ}$ under a pressure of 15 mm.

Wurtz's monhydriododiallyl has the constitution



and boils at $163-165^{\circ}$, with slight decomposition, under the ordinary atmospheric pressure; on treatment with boiling concentrated alcoholic potash, it yields an oil boiling at $64-72^{\circ}$, which is a mixture of two stereoisomeric allylpropenyls, $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$, and dipropenyl. These compounds cannot be separated by fractional distillation, but their tetrabromides can be isolated. When the crude oil boiling at $64-72^{\circ}$ is treated with bromine, it yields besides two crystalline tetrabromides which can be separated with the aid of chloroform, an oily tetrabromide, which does not solidify at -50° , and which is a derivative of allylpropenyl. One of the crystalline products is *dipropenyl tetrabromide*, $\text{CHMeBr}\cdot\text{CHBr}\cdot\text{CH}\cdot\text{CHMeBr}$; it forms flat prisms melting at $182-183^{\circ}$. The second crystalline product is *allylpropenyl tetrabromide*; it forms small plates melting at $63-64^{\circ}$.

A mobile oil, boiling at $77-88^{\circ}$, which probably contains three stereoisomeric *dipropenyls*, $\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHMe}$, and a little *allylpropenyl*, is formed when the crystalline dihydriododiallyl referred to above is treated with concentrated alcoholic potash; the several products cannot be separated by fractional distillation. When the oily mixture is treated with bromine, it gives (a) a tetrabromide, $\text{C}_6\text{H}_{10}\text{Br}_4$, melting at $182-183^{\circ}$, identical with the dipropenyl derivative just mentioned; (b) a tetrabromide, $\text{C}_6\text{H}_{10}\text{Br}_4$, which crystallises in small prisms melting at $95-97^{\circ}$; (c) a tetrabromide, $\text{C}_6\text{H}_{10}\text{Br}_4$, which forms large, clinorhombic plates, and melts at $64-65^{\circ}$; (d) a liquid isomeride. The three crystalline tetrabromides yield one and the same hydrocarbon, namely, dimethyldiacetylene (see below), on treatment with alcoholic potash; they are therefore geometrical isomerides of the constitution $\text{CHMeBr}\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CHMeBr}$, and the hydrocarbon, dipropenyl, from which they are derived, is probably a mixture of three stereochemical isomerides, all of which have the constitution $\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHMe}$. The liquid tetrabromide just referred to gives allenylallylene (see below) and dimethyldiacetylene on treatment with alcoholic potash; the latter is doubtless derived from small quantities of the crystalline tetrabromides, the allenylallylene being probably formed from the liquid tetrabromide of allylpropenyl.

When the crystalline dihydriododiallyl is boiled for a long time with alcoholic potash, an oily tetrabromide is not formed on subsequently treating the product with bromine, because the allylpropenyl, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHMe}$, as was proved by other experiments undergoes intramolecular change into dipropenyl during the first process; this fact, taken in conjunction with the observations of Favorsky (*Bull. Soc. Chim.*, 65, 247) on the intramolecular change undergone by acetylenic hydrocarbons, seems to indicate that when such a change

does occur the molecule becomes more symmetrical, and methy groups are formed at the end of the chain.

Diallyl does not undergo intramolecular change, even when heated with alcoholic potash at 150° , its stability being probably due to the symmetry of its molecule.

When the liquid dihydriododiallyl (see above) is treated with alcoholic potash, it yields an oil boiling at $77-84^{\circ}$, from which tetrabromides identical with those of dipropenyl and of allylpropenyl are obtained; it must, therefore, be regarded as a stereochemical isomeride of the crystalline compound, a view which is in accordance with theoretical considerations.

The oil obtained on treating either of the diallyl tetrabromides with alcoholic potash can be separated by fractional distillation into a portion boiling at $83-88^{\circ}$, consisting of hydrocarbons, a portion boiling at $130-155^{\circ}$, consisting of bromallylallylenes of the constitution $\text{CHBr}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\cdot\text{CH}$ and $\text{CH}_2\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\cdot\text{CH}$, and intermediate fractions which are mixtures of hydrocarbons and bromo-derivatives.

The fraction boiling at $83-88^{\circ}$ partially solidifies at -60° , and consists of dipropargyl, $\text{CH}\cdot\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\cdot\text{CH}$, and a liquid which does not solidify at -50° , which is in all probability a mixture of dipropargyl and allenylallylene (see below).

Dipropargyl melts at -6° , boils at $86-87^{\circ}$, and has a sp. gr. 0.8191 at 0° ; it is a colourless, mobile liquid, and gives with an alcoholic solution of silver nitrate a compound of the composition $\text{C}_6\text{H}_4\text{Ag}_2\cdot 2\text{AgNO}_3$. When heated at about 100° with alcoholic potash, it first undergoes intramolecular change into allenylallylene, but after some hours it is entirely polymerised.

Allenylallylene, $\text{CMe}\cdot\text{C}\cdot\text{CH}_2\cdot\text{C}\cdot\text{CH}$, is obtained when the liquid allylpropenyl tetrabromide (see above) is treated with alcoholic potash. It is a colourless liquid of sp. gr. 0.8250 at 0° , does not solidify at -60° , and boils at $78-83^{\circ}$; it gradually becomes thick when kept, and is rapidly polymerised by alcoholic potash at 100° without formation of dimethyldiacetylene; it combines with silver nitrate in alcoholic solution, yielding a compound of the composition $\text{C}_6\text{H}_5\text{Ag}\cdot\text{AgNO}_3$.

Dimethyldiacetylene, $\text{CMe}\cdot\text{C}\cdot\text{C}\cdot\text{C}\cdot\text{CMe}$, is formed, as already stated, by the action of alcoholic potash on dipropenyl tetrabromide; it can also be obtained by treating propylene with an ammoniacal solution of cuprous chloride and oxidising the product with potassium ferricyanide; the yield is 50 per cent. of the theoretical, assuming that the copper compound has the composition $(\text{C}_3\text{H}_3)_2\text{Cu}_2$. It sublimes very readily in small prisms, melts at 64° , boils at $129-130^{\circ}$, and is specifically lighter than water; it dissolves freely in ether, alcohol, &c., but is almost insoluble in water. It is remarkably stable, and does not explode on percussion; it does not give a precipitate with an ammoniacal solution of cuprous chloride or with the other acetylenic reagents.

The *tetrabromide*, $\text{CMeBr}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CMeBr}$, prepared by treating the hydrocarbon with a chloroform solution of bromine at a temperature below 0° until a permanent coloration is produced, is a crystalline compound melting at 48° , and readily soluble in the ordinary organic

solvents; on treatment with alcoholic potash, or with sodium amalgam, it is reconverted into the original hydrocarbon; no other tetrabromide seems to be formed from dimethyldiacetylene, a result which is in harmony with stereochemical considerations.

An oil boiling at 143—152°, which consists of ketones of the composition C_8H_8O and diketones of the composition $C_8H_{10}O_2$, is formed when finely-divided dimethyldiacetylene is dissolved in well-cooled concentrated sulphuric acid, and the solution poured on to ice; on treating the oil with potash, only the diketones pass into solution. The portion of the oil which is insoluble in potash is a yellowish liquid of sp. gr. 0.9137 at 0°, and boils at 149—150°; it combines with phenylhydrazine and with bromine at the ordinary temperature, and doubtless consists of the ketone $COMe \cdot CH_2 \cdot C \cdot CMe$, mixed possibly with a small quantity of the isomeride $COEt \cdot C \cdot CMe$. The portion of the oil which is soluble in potash is free from acetylacetone, $CH_2Ac \cdot CH_2Ac$, and consists of acetylpropionylmethane, $COEt \cdot CH_2Ac$, mixed possibly with dipropionyl, $COEt \cdot COEt$; on treatment with copper acetate, it yields a copper derivative which crystallises in small, violet prisms melting at 197—198° (see below).

When dimethyldiacetylene is heated at 100° with a dilute alcoholic solution of mercuric chloride, it gradually passes into solution, and, on subsequent distillation, an oil boiling at about 145° is obtained; the alcoholic solution of this oil gives, with a saturated solution of copper acetate, a compound of the composition $C_{12}H_{18}O_4Cu$, which melts at 197—198°, and is identical with the copper derivative of acetylpropionylmethane described by Claisen.

A compound of the composition $C_8H_{12}O$ is formed when dimethyldiacetylene is heated with alcoholic potash at 130°; it is a yellowish liquid of sp. gr. 0.8956 at 0°, has a pleasant ethereal odour, and boils at 169—170° under the ordinary pressure, and at 72—73° under a pressure of 20 mm.; determinations of its vapour density gave results agreeing with those required by a compound of the molecular formula $C_8H_{12}O$, so that the compound is formed by the combination of the hydrocarbon with alcohol.

The heat of combustion of dimethyldiacetylene is 847,384 cal., that of dipropargyl being 853,600 cal., and that of benzene 776,000 cal.

Divinyl glycol, $CH_2 \cdot CH \cdot CH(OH) \cdot CH(OH) \cdot CH \cdot CH_2$, is obtained, together with other products, when acetaldehyde is submitted to the action of a zinc-copper couple in well-cooled, dilute acetic acid solution; it is a colourless oil of sp. gr. 1.0169 at 0°, and boils at 101—102° under a pressure of 10 mm., and at 197—198° under the ordinary atmospheric pressure, apparently without decomposition. It has a bitter taste and a sweet smell, oxidises on exposure to the air, and does not solidify at -60°; it is miscible with water, alcohol, ether, and chloroform in all proportions. The *diacetyl* derivative, $C_{10}H_{14}O_4$, prepared by heating the glycol with acetic anhydride at 150°, is a colourless liquid of sp. gr. 1.0510 at 0°, and boils at 128—129°, under a pressure of 40 mm.; it is insoluble in water, and when heated with alcoholic barium hydroxide it is reconverted into the glycol. Although divinyl glycol contains two asymmetric carbon

atoms, and can, therefore, exist in different geometrical modifications, the glycol obtained in the manner described seems to be the pure inactive compound, free from the racemic modification; the oil recovered from a 1 per cent. solution in which fungi have been cultivated, is optically inactive and identical with the original preparation.

Three *tetrabromides* of the composition $C_6H_{10}Br_4O_2$ are obtained on treating divinyl glycol with bromine in chloroform solution at -15° . One of these crystallises from boiling benzene in acicular prisms, melts at 174° , is only sparingly soluble in boiling benzene, and is stable at 100° ; the second isomeride crystallises from cold benzene, in which it is readily soluble, in silky tufts of needles, melts at $98-99^\circ$, and decomposes below 100° with evolution of hydrogen bromide. The third isomeride is an oil, possibly a mixture.

When either of the crystalline tetrabromides just referred to is dissolved in ether, and finely-divided potash added to the warm solution, a crystalline compound of the composition $C_6H_8Br_2O_2$ is formed, together with a liquid, which is a mixture of various isomerides, and boils at $130-165^\circ$ under a pressure of 20 mm.; the former crystallises in needles or plates, and melts at 102° .

The *tetrabromide*, $C_{10}H_{14}O_4Br_4$, prepared by treating the diacetyl derivative of divinyl glycol with bromine in well-cooled chloroform solution, is a crystalline substance melting at $195-205^\circ$; it is possibly a mixture of geometrical isomerides.

A crystalline compound of the composition $C_6H_8(OH)_4Cl_2$ is obtained, together with a large quantity of oily products, when divinyl glycol is treated with hypochlorous acid in the cold; it separates from boiling water in elongated rhombohedra, optically uniaxial and negative, and melts at $204-206^\circ$ with evolution of hydrogen chloride. It is not identical with the mannitol dichlorohydrin prepared by Bouchardat (*Ann. Chim. Phys.*, **6**, 114); its *tetracetyl* derivative, $C_{14}H_{20}O_8Cl_2$, melts at $169-170^\circ$, that of mannitol dichlorohydrin at $128-130^\circ$.

The *dibromide*, $CH_2\cdot CH\cdot CHBr\cdot CHBr\cdot CH\cdot CH_2$, can be obtained by dissolving divinyl glycol in well-cooled phosphorus tribromide; it crystallises from ether in triclinic prisms, and melts at $84.5-85^\circ$. It combines readily with bromine in well-cooled chloroform solution, yielding a small quantity of a *tetrabromide*, $C_6H_8Br_4$, which crystallises in prisms melting at 112° , and a much larger quantity of an *isomeride*, which crystallises in prisms melting at $103-109^\circ$; these two tetrabromides are also formed when divinyl glycol is poured on to well-cooled phosphorus pentabromide.

The compound $CH_2\cdot CH\cdot CH(OEt)\cdot CH(OEt)\cdot CH\cdot CH_2$ is formed, and not the hydrocarbon $CH_2\cdot CH\cdot C\cdot C\cdot CH\cdot CH_2$, as might have been expected, when the dibromide of divinyl glycol is heated with concentrated alcoholic potash; it is a colourless, sweet-smelling liquid of sp. gr. 0.9110 at 0° , and boils at $111-113^\circ$ under a pressure of 10 mm., and at $224-226^\circ$ under the ordinary atmospheric pressure; it combines with bromine with great energy.

The tetrabromides melting at 112° and $108-109^\circ$ respectively give with alcoholic potash a hydrocarbon which has doubtless the consti-

tution $\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{C}\cdot\text{C}\cdot\text{CH}$; it gives a precipitate with an ammoniacal solution of cuprous chloride and a yellow precipitate with an alcoholic solution of silver nitrate.

F. S. K.

Decomposition of Chloroform in presence of Iodine. By A. BESSON (*Compt. rend.*, 116, 102—103).—Iodine facilitates the decomposition of chloroform by heat. If two tubes, one containing pure chloroform and the other chloroform mixed with a small quantity of iodine, are heated at 250—275° for the same time, the first shows no signs of change, but the second contains carbon, and when opened gives off small quantities of hydrogen chloride and a carbon chloride.

If chloroform vapour containing 1 per cent. of iodine is passed through a tube containing pumice stone heated to incipient redness, the crude product, after separation of unaltered chloroform, has the following composition: carbon dichloride, C_2Cl_4 , 35 per cent.; carbon hexachloride, C_2Cl_6 , 20 per cent.; carbon tetrachloride, CCl_4 , 15 per cent.; hexachlorobenzene, C_6Cl_6 , 10 per cent.; carbon sesquichloride, C_4Cl_6 , 8 per cent., and other products containing a small quantity of the compound C_2HCl_5 and small quantities of iodine compounds. The precise composition of the product depends on the temperature at which decomposition has taken place.

C. H. B.

Synthesis of Mononitroparaffins. By I. BEWAD (*Ber.*, 26, 129—139; compare *Abstr.*, 1891, 653).—When chloropicrin is treated with zinc ethide, the following reactions take place:—(1) $\text{CCl}_3\cdot\text{NO}_2 + 3\text{ZnEt}_2 = \text{CEt}_3\cdot\text{NO}_2 + 3\text{ZnEtCl}$; (2) $\text{CCl}_3\cdot\text{NO}_2 + 3\text{ZnEt}_2 = \text{CHEt}_2\cdot\text{NO}_2 + 3\text{ZnEtCl} + \text{C}_2\text{H}_4$; (3) $\text{CCl}_3\cdot\text{NO}_2 + 3\text{ZnEt}_2 = \text{CH}_2\text{Et}\cdot\text{NO}_2 + 3\text{ZnEtCl} + 2\text{C}_2\text{H}_4$; (4) $\text{CCl}_3\cdot\text{NO}_2 + 3\text{ZnEt}_2 = \text{CH}_3\cdot\text{NO}_2 + 3\text{ZnEtCl} + 3\text{C}_2\text{H}_4$. Zinc methide acts on halogen nitroparaffins in a similar manner, except that it does not bring about the formation of an unsaturated hydrocarbon; in the case of bromonitropropane, for example, the following equations express the various actions:—(1) $\text{CMe}_2\text{Br}\cdot\text{NO}_2 + \text{ZnMe}_2 = \text{CMe}_3\cdot\text{NO}_2 + \text{ZnMeBr}$; (2) $\text{CMe}_2\text{Br}\cdot\text{NO}_2 + \text{ZnMe}_2 = \text{CMe}_2(\text{ZnMe})\cdot\text{NO}_2 + \text{MeBr}$. The zinc compound formed in the latter case is decomposed on treatment with water with evolution of methane:— $\text{CMe}_2(\text{ZnMe})\cdot\text{NO}_2 + 2\text{H}_2\text{O} = \text{CHMe}_2\cdot\text{NO}_2 + \text{Zn}(\text{OH})_2 + \text{CH}_4$. Since the above reactions occur in the case of other simple bromo- and chloro-nitroparaffins, the synthesis of the higher nitroparaffins can be readily accomplished. For this purpose, the zinc alkyl derivative and some dry ether are placed in a flask filled with carbonic anhydride and cooled with ice cold water, and the halogen nitrocompound, or its ethereal solution, gradually added; after keeping for a few days, first in the cold and then at the ordinary temperature, the mixture is carefully treated with water, the products distilled with steam, the distillate acidified with hydrochloric acid, and the ethereal solution separated; the several compounds are separated by the aid of potash or by fractional distillation, or by a combination of these two processes.

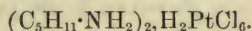
Secondary nitropropane, $\text{CHMe}_2\cdot\text{NO}_2$, prepared from bromonitroethane and zinc methide, is a liquid of sp. gr. 1.024 at 0°, and boils at

117—120°. On reduction with zinc and sulphuric acid, it is converted into an amine, the platinochloride of which has the composition $(\text{NH}_2\text{Pr}^{\beta})_2, \text{H}_2\text{PtCl}_6$. The identity of the nitropropane with the compound prepared by V. Meyer's method was proved by converting it into propylpseudonitrol, melting at 76°. The bromo-derivative, $\text{CBrMe}_2\cdot\text{NO}_2$, is a neutral oil of sp. gr. 1.6562 at 0°, and boils at 151—153° under a pressure of 712 mm.

Secondary nitrobutane, $\text{CHMeEt}\cdot\text{NO}_2$, is formed, together with nitroethane, when bromonitroethane is treated with zinc ethide; it is a liquid of sp. gr. 0.9877 and boils at 138—139° under a pressure of 747 mm.; it can be converted into butylpseudonitrol, melting at 58°, and into an amine, the platinochloride of which has the composition $(\text{C}_4\text{H}_9\cdot\text{NH}_2)_2, \text{H}_2\text{PtCl}_6$.

Tertiary nitrobutane, $\text{CMe}_3\cdot\text{NO}_2$, can be prepared by treating bromonitropropane, dibromonitroethane, or chloropicrin with zinc methide; when dibromonitroethane is employed, secondary nitropropane and nitroethane are also formed. The properties of this substance have been described (*loc. cit.*).

Tertiary *nitropentane*, $\text{CMe}_2\text{Et}\cdot\text{NO}_2$, is formed, together with ethylene and secondary nitropropane, when secondary bromonitropropane is treated with zinc ethide; it is also produced when secondary bromonitrobutane is treated with zinc methide, being accompanied in this case by secondary nitrobutane. It is a colourless, mobile liquid of sp. gr. 0.9783 at 0°, and boils at 149—151° under a pressure of 748 mm.; on reduction with tin and hydrochloric acid, it is converted into an amine, the *platinochloride* of which has the composition



Tertiary *nitrohexane*, $\text{CMeEt}_2\cdot\text{NO}_2$, is formed, together with secondary nitrobutane and nitroethane, by the action of dibromonitroethane on zinc ethide; it is a colourless liquid of sp. gr. 0.9775 at 0°, and boils at 170—172° under a pressure of 749 mm.; it is insoluble in alkalis, and does not react with bromine or with nitrous acid.

Tertiary *nitroheptane*, $\text{CEt}_3\cdot\text{NO}_2$, secondary nitropentane, primary nitropropane, and nitromethane are produced by the action of zinc ethide on chloropicrin. The tertiary nitroheptane was not obtained in a pure condition; the impure substance is insoluble in potash, does not react with bromine or with nitrous acid, and on reduction is converted into a base, the *platinochloride* of which has the composition $(\text{C}_7\text{H}_{15}\cdot\text{NH}_2)_2, \text{H}_2\text{PtCl}_6$. Secondary *nitropentane*, $\text{CHEt}_2\cdot\text{NO}_2$, is a colourless, mobile, pleasant smelling liquid of sp. gr. 0.9757 at 0°, and boils at 152—155° under a pressure of 746 mm.; it forms a sodium derivative which is only very sparingly soluble in alcohol, and its alkaline solution gives with nitrous acid a colourless, crystalline *amylpseudonitrol*, melting at 66° with decomposition; on reduction, it is converted into an amine, the *platinochloride* of which has the composition $(\text{C}_5\text{H}_{11}\cdot\text{NH}_2)_2, \text{H}_2\text{PtCl}_6$. The bromo-derivative, $\text{C}_5\text{H}_{10}\text{Br}\cdot\text{NO}_2$, is a yellowish oil of sp. gr. 1.4562; it is insoluble in water and alkalis.

F. S. K.

Methyl and Ethyl Alcohol as Solvents. By C. A. LOBEY DE BRUYN (*Zeit. physikal. Chem.*, **10**, 782—789; *Rec. Trav. Chim.*, **11**, 112—157; and *Ber.*, **26**, 268—274).—The author confirms in the first instance the rule given by Dumas and Péligot that methyl alcohol occupies a position as a solvent intermediate between that of water and ethyl alcohol. Exceptions to this rule are offered by hydrogen chloride, mercuric chloride and iodide, the aromatic nitro-compounds, nitroglycerol, and collodion-cotton, which are more soluble in methyl alcohol than in water or ethyl alcohol. A curious and unexpected behaviour was encountered in the case of salts containing water of crystallisation, and more especially noticeable in the case of sulphates of the dyad metals. These are soluble in methyl alcohol, in some cases to a very considerable extent, but the solutions formed are unstable, and deposit the salt again on standing. The addition of a few drops of water accelerates the deposition, so that the salts are less soluble in methyl alcohol containing water than in methyl alcohol alone. The salt separating from the solution generally contains less water of crystallisation than that originally dissolved, and, in some cases, a replacement of a portion of the water by the alcohol is found to have taken place.

The author points out that methyl alcohol might in many cases be used with advantage in place of ethyl alcohol in the laboratory as a solvent. It does not oxidise so readily, nor is it so susceptible to the action of chlorine, bromine, and iodine. In many cases reagents, such as sodium, potassium cyanide, ammonia, and hydroxylamine, are found to be more soluble in methyl than in ethyl alcohol, and solutions in the former are, therefore, to be preferred to solutions in the latter.

H. C.

Pinacone and its Derivatives. By F. COUTURIER (*Ann. Chim. Phys.* [6], **26**, 433—501).—The following experiments were undertaken with the object of proving or disproving the supposed identity of the chloro-derivatives of pinacone and pinacolone.

When anhydrous pinacone is treated with phosphorus oxychloride, it yields pinacolone and a small quantity of a compound of the constitution $\text{OH} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \text{Cl}$, which is identical with the chlorhydrin obtained by Eltekow (*Ber.*, **16**, 399) by the union of hypochlorous acid with tetramethylethylene.

The dichloro-derivative, $\text{CMe}_2 \text{Cl} \cdot \text{CMe}_2 \text{Cl}$, is formed in small quantity when pinacone is treated with phosphorus trichloride in the cold; it is a crystalline compound, sublimes very readily, melts at 160° when heated in a sealed capillary tube, and is identical with the dichlorodiisopropyl described by Schorlemmer (*Annalen*, **144**, 184). The corresponding dibromo-derivative, $\text{C}_6\text{H}_{12}\text{Br}_2$, prepared in like manner, crystallises in long prisms, sublimes readily, and melts at $173\text{—}174^\circ$ with partial decomposition when heated in a sealed tube; it does not react with hydroxylamine, and, when heated with alcoholic potash, it is immediately converted into tetramethylethylene with elimination of 2 atoms of bromine; when heated with water and silver oxide, it yields pinacone, whereas potassium carbonate converts it into a mixture of pinacone and pinacolone.

The *dibromo*-derivative, $\text{CMe}_3\cdot\text{CMeBr}_2$, is formed when pinacolone is treated with phosphorus tribromide in the cold; it sublimes readily, and melts at 187° when heated in a sealed tube. The corresponding *dichloro*-derivative, prepared in like manner, is reconverted into pinacolone when heated with water at 100° ; it reacts with hydroxylamine, yielding a crystalline *oxime*, $\text{CMe}_3\cdot\text{CMe}\cdot\text{NOH}$, which melts at 74° .

Diacetylpinacone, $\text{C}_6\text{H}_{12}(\text{OAc})_2$, is formed when pinacone is mixed with acetic anhydride, and the mixture kept for a long time at the ordinary temperature; it is a colourless, crystalline compound, and melts at 65° . When pinacone is heated at 90 – 95° with acetic anhydride, it is converted into β -dipropylene (Abstr., 1891, 282) and other products, only a very small quantity of the diacetyl derivative being formed.

The alcohol of the composition $\text{C}_6\text{H}_{14}\text{O}$, obtained by reducing pinacolone, combines with acetic acid forming an acetate; from the results of determinations of the initial velocity and limit of etherification, it would seem that the compound in question is a secondary alcohol, a view which is supported by the fact that not a trace of an unsaturated hydrocarbon is formed during the process.

Pinacolyl chloride, $\text{CMe}_3\cdot\text{CHMeCl}$, prepared by treating the alcohol just referred to with hydrogen chloride, undergoes complete dissociation at 100° into hydrogen chloride and hydrocarbon, combination taking place again on cooling. The corresponding *bromide*, $\text{CMe}_3\cdot\text{CHMeBr}$, melts at 24 – 25° , and boils at 132° with partial decomposition under a pressure of 758 mm.; it undergoes partial dissociation at 100° , but even at 183° the process is not complete. β -Hexyl chloride does not dissociate at 130° .

Pseudobutylethylene, $\text{CMe}_3\cdot\text{CH}\cdot\text{CH}_2$, is formed, together with tetramethylethylene, when pinacolyl bromide is heated with finely divided potash; it is a colourless liquid of sp. gr. 0.6795 at 0° , boils at 56 – 58° , and combines with bromine, yielding a liquid *dibromide*, $\text{C}_6\text{H}_{12}\text{Br}_2$, which does not solidify at -23° .

Pseudobutylethylene glycol, $\text{CMe}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, prepared by oxidising the hydrocarbon with potassium permanganate, is a colourless, viscous liquid of sp. gr. 0.9986 at 0° ; it boils at 197° under a pressure of 755 mm., and is miscible with water and ether in all proportions. The *diacetyl* derivative, $\text{C}_6\text{H}_{12}(\text{OAc})_2$, boils at 217 – 218° under a pressure of 760 mm.

Tetramethylethylene is readily oxidised by potassium permanganate yielding pinacone; the formation of tetramethylethylene from pinacolyl bromide by the action of potash is, doubtless, the result of intramolecular change; aqueous ammonia at 100° converts pinacolyl bromide into tetramethylethylene only, so that this reaction can be conveniently employed for the preparation of the pure hydrocarbon.

β -Dipropylene (*loc. cit.*) is converted into pinacolone when heated with very dilute sulphuric acid at 100° ; it combines with nitric peroxide in ethereal solution, yielding a compound of the composition $\text{C}_6\text{H}_{10}(\text{NO}_2)_2$, which crystallises in colourless needles melting at 72 – 73° .

The pinacone, $\text{C}_{12}\text{H}_{26}\text{O}_2$, which is obtained as a bye-product in the

reduction of pinacoline, is decomposed by dilute sulphuric acid into tetramethylethylene and pinacoline. F. S. K.

Bye-products of the Action of Sodium Hydroxide on Glycerol. By L. RAISONNIER (*Bull. Soc. Chim.* [3], 7, 554).—In the preparation of propylene glycol by the action of soda on glycerol, Fernbach (Abstr., 1881, 145) obtained as bye-products, methyl, ethyl, and propyl alcohols. The author has recognised the presence of the first two, but has not succeeded in isolating propyl alcohol from the bye-product; he has, however, separated a small quantity of allyl alcohol. A. R. L.

Supposed Secondary Hexyl Alcohol from Mannitol. By A. COMBES and LE BEL (*Bull. Soc. Chim.* [3], 7, 551–552).—Erlenmeyer succeeded in converting hexyl iodide from mannitol into an alcohol which, from a study of its decomposition products, he supposed to be a secondary alcohol. When a 0.5 per cent. solution of this alcohol is submitted to the action of *Penicillium glaucum*, the solution, on concentration, was found to be dextrorotatory. Now this result is surprising, inasmuch as it has been shown by one of the authors that methylpropylcarbinol and methylethylcarbinol give lævorotatory solutions after the action of *Penicillium glaucum*.

The authors next prepared methylbutylcarbinol by the hydrogenation of methyl butyl ketone, obtained by decomposing propylacetylacetone, $\text{COMe}\cdot\text{CHPr}\cdot\text{COMe}$, with potash. By cultivating *Penicillium glaucum* in a solution of the alcohol so prepared, a lævorotatory liquid was obtained, as might have been expected.

Finally, ethylpropylcarbinol was prepared by distilling a mixture of calcium butyrate and propionate, and hydrogenising the resulting ethyl propyl ketone. A solution of this alcohol, like one of that prepared from mannitol, became dextrorotatory after cultivating *Penicillium glaucum* in it, so that there can be no doubt that the alcohol from mannitol is ethylbutylcarbinol. The chloride derived from the last-named alcohol is lævorotatory, and the iodide is dextrorotatory in accordance with Guye's theory. A. R. L.

Pentacetyl Derivatives of Glucose (Dextrose). By A. P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 11, 106–111).—The compound of melting point 134° , obtained by heating a mixture of glucose and sodium acetate with acetic anhydride, is a pentacetylglucose, and not an octacetyldiglucoose, as stated by Herzfeld and by Erwig and Königs; it is optically inactive. The author confirms Erwig and Königs's observation (Abstr., 1889, 952) that a pentacetylglucose, melting at 112° , is produced by heating glucose with acetic anhydride and zinc chloride; it is much more soluble in water and alcohol than the first-mentioned isomeride, besides which it is feebly dextrorotatory. Both compounds yield glucose on hydrolysis with aqueous ammonia, and the author hopes later to be able to explain their isomerism. He suggests that the decacetyldiglucoheptose obtained by Fischer (Abstr., 1892, 1167) may turn out to be a hexacetylglucoheptose. Fischer's analytical values agree equally well with those

demanding for the last-named compound, and he did not make an acetyl determination.

A. R. L.

Chloralose, a Derivative of Chloral, and its Physiological Properties. By HANRIOT and C. RICHET (*Compt. rend.*, 116, 63—65).—Equal quantities of anhydrous chloral and dry glucose are heated together at 100° for an hour, and the cooled product is mixed with a small quantity of water and extracted with boiling ether. The portion soluble in ether is distilled repeatedly with water until all chloral is expelled, and the aqueous solution is then subjected to fractional crystallisation; in this way, the anhydroglucochloral which has already been described by Heffter (*Abstr.*, 1889, 845), and which the authors propose to call *chloralose*, is obtained in two forms, namely, chloralose, which crystallises in slender needles melting at 184—186°, and volatilising without decomposition, and *parachloralose*, which crystallises in nacreous lamellæ melting at 229°. The latter is soluble with difficulty even in hot water. Both substances have the composition $C_8H_{11}Cl_3O_6$.

Chloralose with sulphuric acid yields a disulphonic derivative, and with acetic anhydride a tetracetyl derivative. Contrary to the statement of Heffter, it does not yield glucose when treated with potassium hydroxide.

Parachloralose, probably by reason of its insolubility, is without physiological activity, but chloralose, when administered by ingestion, produces hypnotic effects, and at the same time increases the excitability of the spinal marrow. When given to dogs in the proportion of 0.6 gram per kilogram of body weight, it produces only anæsthesia, and not death. The hypnotic effect begins to be evident with doses so small as 0.02 gram per kilogram of body weight, and hence chloralose is much more active than chloral, and its effect cannot be attributed to a decomposition into chloral. When administered to human beings in doses of from 0.2 gram to 0.75 gram, but not exceeding 1 gram, it acts as a valuable hypnotic, producing no disturbance of digestion, no cephalalgia, and no phenomena of intoxication.

C. H. B.

Soluble Pentoses in Plants. By G. DE CHALMOT (*Amer. Chem. J.*, 15, 21—38).—The same reasoning which tends to show that hexoses in plants are built up in the leaves from formaldehyde also holds good for pentoses, and it is probable that the pentosans found in other parts of the plants as constituents of the cell-walls are formed from pentoses in the places where they are found. Hence these pentoses must be soluble. To test this, the leaves of a large number of plants representative of most classes and orders were extracted with water, the extract, after purification with lead acetate, distilled with 12 per cent. hydrochloric acid, and the distillate tested with aniline acetate for furfuraldehyde. The latter was found in every case, although in some cases in very small quantity. To determine whether an amount of furfuraldehyde sufficient to mask these results would be yielded by hexoses under this treatment, the furfuraldehyde obtained both from the leaves and from a known quantity

of invert sugar was estimated by a colorimetric method based on the formation of the red dye $2\text{NH}_2\text{Ph}, \text{C}_5\text{H}_4\text{O}, \text{HCl}, \text{H}_2\text{O}$ when aniline and furfuraldehyde are added to alcoholic acetic acid. The result showed that invert sugar yields only 0.2 per cent. of furfuraldehyde, which, calculated on the hexoses present, in trefoil for instance (0.89 per cent.), would correspond with only 0.002 per cent. of furfuraldehyde from the trefoil, which actually yielded, however, 0.1 per cent. In all cases similar results were obtained, and the quantity of hexoses present was insufficient to account for the formation of the furfuraldehyde, which presumably, therefore, arose from soluble pentoses.

The actual amount (at the most 0.5 per cent.) of these pentoses in the leaves and colourless bark of plants is small compared with that of the hexoses, of which as much as 1.8 per cent. may be present. The pentoses readily diffuse through membranes, and are therefore presumably simple sugars of the composition $\text{C}_5\text{H}_{10}\text{O}_5$.

In many plants, a larger quantity of pentoses is present in the evening than in the morning, so that, like the hexoses, they are probably converted into temporary solid forms immediately after their formation.

JN. W.

Xylose. By G. BERTRAND (*Bull. Soc. Chim.* [3], 7, 499—502).—Xylose occupies an important place in the vegetable kingdom, since it is invariably found amongst the decomposition products of the incrusting substances of the angiosperms. It frequently crystallises in prisms, belonging to the orthorhombic system, which polarise light. 100 parts of water at 20.3° dissolve 117.05° parts of xylose; it is insoluble in absolute alcohol, but 10 c.c. of a solution in 90 per cent. alcohol, saturated at 19° , were found to contain 0.3.9 gram of the sugar. The rotatory power in a solution approximating 10 per cent. concentration was found to be $[\alpha]_D = +19.4^\circ$ at 23° (compare Wheeler and Tollens, *Annalen*, 254, 309; Hébert, *Abstr.*, 1890, 1460). Xylose is not fermentable with yeast, and its cupric reducing power (Fehling's solution) is 109.6 per cent. that of glucose, or 10.4 per cent. that of invert sugar. When either xylose or arabinose is gently heated with a small quantity of hydrochloric acid, furfuraldehyde is produced which gives, on addition of a little orcinol, a violet-blue coloration; under the same conditions, the hexoses give an orange-red coloration. When xylose is allowed to remain for 24 hours in contact with 30—50 times its weight of bromine water, the excess of bromine expelled by boiling, and cadmium carbonate added, the addition of an equal volume of alcohol to the concentrated filtrate gives a compound, $\text{C}_5\text{H}_8\text{O}_6 \cdot \text{CdBr} + \text{H}_2\text{O}$, which crystallises in prismatic needles, and has no melting point, but swells up when heated: the formation of this compound is characteristic of xylose.

A. R. L.

Sugar from Pear Pectose. By R. W. BAUER (*Landw. Versuchs-Stat.*, 41, 477).—Pear pectose (5 grams, containing 4.731 grams of dry matter), when boiled with 2 per cent. sulphuric acid for four hours, gave a filtrate which polarised $+12^\circ$ with 100 mm. The solution was made up to 200 c.c. with absolute alcohol, and neutralised with calcium carbonate. The solution polarised $+2^\circ$; it contained 0.5955 gram of sugar crystals and optically active gum. This

gave, with phenylhydrazine, an osazone crystallising in stellate groups of microscopic needles melting at 195° . The needles are pleochroic, and give a slightly dextrorotatory solution in glacial acetic acid. The compound is, therefore, probably galactosazone.

N. H. M.

Inversion of some Carbohydrates. By E. WINTERSTEIN (*Landw. Versuchs-Stat.*, **41**, 375—384).—The object of the experiments, which were made with stachyose and with lupeose (β -galactan), was to ascertain the amount of acid and the length of time necessary to bring about complete inversion; also to determine the amounts of glucose formed. Determinations were also made with raffinose, wood-gum (from beech-wood meal; Wheeler and Tollens), and with cellulose (pure cotton wool extracted with 0.5 per cent. aqueous soda, and a preparation from lupin hulls).

The substance, dried at 105 — 110° , was boiled with a known volume of dilute sulphuric acid, the whole made up to a definite bulk, and the glucose determined in a portion by Allihn's method. The results are calculated as if dextrose alone were present, using Allihn's grape sugar tables. The error is only slight, as the reducing power of the known glucoses does not differ much.

With stachyose, the best results, 74.52 per cent. of the theoretical amount, were got by boiling for one hour with 2 per cent. hydrochloric acid; with lupeose, under the same conditions, 78.63 per cent. was obtained. In the case of raffinose, one hour's heating with N/5 hydrochloric acid gave the highest yield (86.78 per cent.). Wood-gum gave the highest percentage (77.92) when boiled with 2 per cent. acid for one hour.

Cotton-wool cellulose (0.9668 gram dry and free from ash) was treated with concentrated sulphuric acid (5 grams) and, after 12 hours, diluted with water, filtered, and diluted to 200 c.c. This was boiled for two hours in a reflux apparatus. 92.40 per cent. of the theoretical amount was obtained. Lupin-hull cellulose treated in the same way gave 93.81 per cent. Longer boiling gave rather lower results.

N. H. M.

Preparation and Purification of the Propylamines. By F. CHANCEL (*Bull. Soc. Chim.* [3], **7**, 405—407).—A mixture of propylamine (45 parts), dipropylamine (35 parts), and tripropylamine (20 parts) is obtained by heating propyl chloride and aqueous ammonia (equal mols.) dissolved in alcohol for 10 hours at 100 — 110° , in a closed vessel. The three bases are separated by fractional distillation, and are then purified as follows:—Propylamine is converted into dipropyloxamide by treatment with ethyl oxalate; propylamine picrate melts at 135° . Dipropylamine is converted into dipropyloxamic acid by means of oxalic acid. Tripropylamine is purified by crystallising its picrate.

A. R. L.

Thionyl-diethylhydrazone. By A. MICHAELIS and O. STORBECK (*Ber.*, **26**, 310—311).—*Thionyl-diethylhydrazone*, $\text{NET}_2\cdot\text{N}\cdot\text{SO}$, is obtained by adding an ethereal solution of thionyl chloride to an ice-cold ethereal solution of diethylhydrazine. It is a colourless oil, having

a faint aromatic odour, distils undecomposed at 73° under 20 mm. pressure, and is gradually decomposed by water. When treated with sodium hydroxide, it yields hydrazine; with dilute sulphuric acid, it yields sulphurous anhydride.

E. C. R.

The Alleged Optical Activity of Chlorofumaric acid. An Active Chlorosuccinic acid. By P. WALDEN (*Ber.*, 26, 210—215).—Perkin states (*Trans.*, 1888, 695) that ethyl chlorofumarate and chloromaleate exhibit a slight optical activity ($+6'$)*. This case of optical activity among unsaturated compounds is not easily reconciled with Van't Hoff's hypothesis, according to which such activity is conditioned by the presence of an "asymmetric" carbon atom. The author, therefore, has investigated the matter more closely, and finds that when phosphorus pentachloride is allowed to act on tartaric acid, the temperature never being allowed to rise above 60° , a mixture of chlorofumaric and dichlorosuccinic acids were obtained, but these are both entirely devoid of optical activity.

Another fact which somewhat impairs the generality of Van't Hoff's hypothesis is that, when, in many active compounds, hydroxyl is replaced by a halogen, the resulting substance is inactive. This is not always the case, however, for the author finds that, when phosphorus pentachloride is allowed to act on malic acid at a temperature not exceeding 55° , fumaric acid and a new *dextrorotatory chlorosuccinic acid*, $C_4H_5ClO_4$, are obtained. It is a white substance, has in the mean $[\alpha]_D = +20.9^{\circ}$, and melts at 174° with evolution of hydrogen chloride and formation of fumaric acid.

C. F. B.

Electrolysis of Trichloroacetic acid. By K. ELBS (*J. pr. Chem.* [2], 47, 104).—By the electrolysis of an aqueous solution of zinc or sodium trichloroacetate, crystals of a compound, which decomposes with evolution of carbonyl chloride and hydrogen chloride, have been obtained. Its properties indicate that it is a derivative of trichloromethyl alcohol; but they do not agree with those of trichloromethyl trichloroacetate.

A. G. B.

Glycolide and its Homologues. By C. A. BISCHOFF and P. WALDEN (*Ber.*, 26, 262—265).—*Glycolide*, $C_4H_4O_4$, is obtained by the distillation of sodium bromoacetate in a vacuum, and crystallises in large, lustrous plates which melt at 86 — 87° ; when heated with water, glycollic acid is formed, whilst with aniline, glycollic anilide is obtained. The yield is 25 per cent. of the salt employed.

The compound hitherto termed glycolide is a polymeride of the preceding substance, and is formed from it by heating it alone or with a trace of zinc chloride; on distillation in a vacuum, glycolide is regenerated. Sodium chloroacetate behaves like the bromoacetate.

By the distillation of sodium bromopropionate, either in a vacuum or under the ordinary pressure, the corresponding lactide is obtained.

* The author seems to have consulted the *Jahresbericht*, not the original paper, in which Perkin says (p. 701), "It is difficult to say whether this rotation is due to the pure ether or not, but it appears to be so." [EDITORS.]

The lactide of hydroxybutyric acid, $\begin{array}{c} \text{CO}-\text{O}-\text{CHEt} \\ | \\ \text{CHEt}\cdot\text{O}\cdot\text{CO} \end{array}$, together with a little crotonic acid, is obtained in a similar manner from sodium α -bromobutyrate; it boils at $257-258^\circ$ under a pressure of 760 mm., melts at $21-22^\circ$, and has a sweet taste.

On distillation, sodium α -bromisobutyrate yields α -hydroxyisobutyric acid, methacrylic acid, and its polymeric modification.

The authors consider that the above results tend to confirm the dynamic hypothesis, since they have failed to obtain closed chain compounds containing four methyl groups. J. B. T.

Action of Potassium Permanganate on Organic Acids. By A. LUMIÈRE and A. SEYEWETZ (*Bull. Soc. Chim.* [3], 7, 538—542). The authors state that potassium permanganate acts in the cold on numerous easily oxidisable organic acids, giving rise to a hydrated manganese dioxide, soluble in an excess of the acid with the production of manganic salts, which latter they propose to study.

When the permanganate is added to oxalic acid in the cold, the following reaction occurs:— $2\text{KMnO}_4 + 3\text{H}_2\text{C}_2\text{O}_4 = 2\text{MnO}_2 + \text{H}_2\text{O} + \text{K}_2\text{CO}_3 + 2\text{H}_2\text{O} + 5\text{CO}_2$. In the presence of an excess of the acid, and when the temperature is kept below $30-40^\circ$, a brownish-red liquid, which has all the properties of a solution of a manganic salt, is formed; the following equation probably represents the reaction:— $2\text{MnO}_2 + 4\text{H}_2\text{C}_2\text{O}_4 = (\text{C}_2\text{O}_4)_3\text{Mn}_2 + 2\text{CO}_2 + 4\text{H}_2\text{O}$. On heating the last-mentioned solution to 60° , or on exposing it to light, it is decolorised, and manganous oxalate separates. The same solution acts as an energetic oxidising agent, and if paper coated with gelatin is impregnated with it, and then plunged into a salt of an amine, colorations which vary according to the nature of the amine are produced. No coloration is produced, however, when the impregnated paper has been exposed to light before treating it with the amine. These properties, which are exhibited also by inorganic manganic salts, have been utilised by Lumière for a new photographic process (*Bull. Soc. franc. fotogr.*, 1892). A. R. L.

Asymmetrical Dicarboxylic acids. By J. W. BRÜHL and R. BRAUNSCHWEIG (*Ber.*, 26, 337—345).—In view of the results obtained by the authors in the etherification of camphoric acid (this vol., i, 277), they have examined the behaviour of other asymmetrical dicarboxylic acids under similar conditions, and have selected in the first place pyrotartaric acid (methylsuccinic acid). The *dimethyl* salt, $\text{C}_5\text{H}_6\text{O}_4\text{Me}_2$, is obtained in the usual manner, and may be separated from the acid salts simultaneously formed by fractionation in a vacuum, or by treatment with alkalis, which readily hydrolyse the latter substances. It is a colourless liquid, which has a faint pleasant odour, and boils at 197° under 759 mm. pressure, and at 101° under 22 mm. pressure. The *diethyl* salt, $\text{C}_5\text{H}_6\text{O}_4\text{Et}_2$, was obtained in a similar manner, and boils at 218° under 759 mm. pressure, and at 125° under 33 mm.

The acid alkyl salts may be obtained by the methods employed in the case of camphoric acid (*loc. cit.*); *orthomethyl pyrotartrate*,

$C_5H_7O_4Me$, is formed by boiling the anhydride with methyl alcohol and is a thick, colourless acid liquid, which is quickly hydrolysed by water, and immediately by alkalis, and boils at $153-153.5^\circ$ under 20 mm. pressure. The *sodium* salt of the same methyl derivative is obtained by heating together the anhydride and a solution of sodium methoxide in methyl alcohol, or by adding sodium to a solution of the anhydride in methyl alcohol. *Orthoethyl pyrotartrate*, $C_5H_7O_4Et$, is obtained in a similar manner, and forms a colourless, odourless oil, which boils at $160-161^\circ$ under 22 mm. pressure, and is also hydrolysed with great ease.

An attempt was next made to prepare the "allo-" methyl ether by treating the dimethyl salt with the requisite quantity of potash dissolved in ethyl alcohol, but it was found that, instead of the potassium methyl salt, potassium ethyl pyrotartrate was formed, the methyl group being replaced by the ethyl group in the course of the reaction. The latter compound may also be obtained by the action of alcoholic potash on the diethyl salt, and agrees in its physical properties with the salt obtained from the anhydride and ethyl alcohol; the authors nevertheless do not regard it as impossible that these two compounds are in reality isomeric.

When ethyl orthopyrotartrate is treated with methyl iodide and sodium methoxide in methyl alcohol solution, it is converted into methyl orthoethyl pyrotartrate, $C_5H_6O_4MeEt$, which is a colourless mobile liquid boiling at $101-102^\circ$ under 20 mm. pressure, and not quite constantly about 198° under 754.1 mm. An attempt to obtain the isomeric orthomethyl ethyl pyrotartrate by the action of ethyl bromide and sodium ethoxide on orthomethyl pyrotartrate in ethyl alcohol solution resulted in the formation of the diethyl salt, the methyl group being in this case also displaced by the ethyl group. A second attempt to prepare it by the action of sodium ethoxide (1 mol.) and ethyl bromide (1 mol.) on a solution of pyrotartaric anhydride in methyl alcohol was likewise unsuccessful, the product being in this case the dimethyl salt.

The spectrometric constants of all the above derivatives were determined, and found to agree closely with the theoretical numbers. Even without the analytical details, the spectrometric investigation was quite sufficient to determine the purity of the compound, and to indicate its nature, even when the action proceeded in an unexpected manner.

H. G. C.

Metahydroxyuvitic acid. By H. MEISTER (*Ber.*, 26, 354-356).—The author has succeeded in preparing the diethyl salt of this acid, $OH \cdot C_6H_2Me(COOEt)_2$, in four different ways, and does not find that it is nearly as unstable as stated by Oppenheim and Pfaff (this Journ., 1874, 1161). It crystallises in plates, melts at 45° , boils at $242-243^\circ$ under 10 mm. pressure, and at $280-310^\circ$ with partial decomposition at the ordinary pressure; the pure compound crystallises from the distillate even in the latter case.

When treated with the theoretical quantity of sodium or potassium ethoxide, it is converted into the ethyl sodium or ethyl potassium salt, which on boiling with water yields the *monethyl salt*, $C_{11}H_{12}O_5$;

this crystallises in white needles melting at 176—177°, and yields a white, curdy *silver* salt on the addition of silver nitrate.

H. G. C.

Butanetetracarboxylic acid. Synthesis of Pentamethylene Derivatives. By K. AUWERS (*Ber.*, **26**, 364—378; compare *Abstr.*, 1891, 546).—By the action of ethyl sodiomalonate on ethyl aconitate in alcoholic solution and subsequent hydrolysis of the product by means of hydrochloric acid, a mixture is obtained consisting of butanetetracarboxylic acid, ketopentamethylenedicarboxylic acid, together with a third acid which melts at 185° with evolution of gas, and is being further investigated. The acids are separated and purified by crystallisation from water.

Butanetetracarboxylic acid melts at 244°, and has been previously prepared by Bischoff from ethyl butanehexacarboxylate; the acid is not affected by potassium permanganate in alkaline solution. The *silver, copper, lead, and barium salts* are sparingly soluble.

The *anhydride*, $O < \begin{array}{c} \text{CO} \cdot \text{CH} - \text{CH} \cdot \text{CO} \\ \text{CO} \cdot \text{CH}_2 \quad \text{CH}_2 \cdot \text{CO} \end{array} > O$, is prepared by the action of acetic chloride on the acid at 100°, and crystallises from acetone, on the addition of light petroleum, in lustrous plates which melt at 172—173°.

Ketopentamethylenedicarboxylic acid, $\text{CO} < \begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \end{array}$, is deposited in octahedral crystals melting at 189°, and appears to be formed by the elimination of water and carbonic anhydride from butanetetracarboxylic acid; this is analogous to the production of ketopentamethylene from calcium adipate, and of methyl- and dimethyl-ketopentamethylene from β -methyladipic acid and $\alpha\alpha$ -dimethyladipic acid respectively. The *silver, lead, mercury, copper, barium, calcium, and ferric salts* are sparingly soluble. The *dimethyl salt* crystallises from light petroleum in colourless, flat, feathery needles melting at 63—64°. The *diethyl salt* is liquid at ordinary temperatures, and yields an *oxime* which crystallises from dilute alcohol in silky, lustrous, concentric needles melting at 74°. The *phenylhydrazone* of the ethyl salt is deposited from alcohol in yellow needles which melt at 105° and decompose spontaneously.

Ketopentamethylenedicarboxylic acid, when heated at 230—260° under a pressure of 30—40 mm., yields an acid crystallising in slender needles; it melts at 140°, and is being further investigated. By the oxidation of the carboxylic acid with potassium permanganate in alkaline solution, or with nitric acid, oxalic acid is produced.

By the action of ethyl sodioethylenetricarboxylate on ethyl aconitate, and subsequent hydrolysis of the ethereal salt, succinic acid is obtained as the sole product.

J. B. T.

Dipropylcarbamide and Dipropylthiocarbamide. By F. CHANCEL (*Compt. rend.*, **116**, 62—63).—When propyl isocyanate is added to an aqueous solution of propylamine, there is immediate reaction with considerable development of heat. A mixture of propyl isocyanate and propyl iodide may be used, and the dipropylamide hydr-

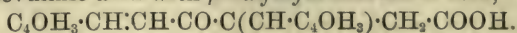
iodide that is then formed may be separated from the dipropylcarbamide by washing with cold water, in which it is much the more soluble.

The symmetrical dipropylcarbamide thus obtained, crystallises from hot water in white plates with a micaceous lustre. It melts at 104° and boils at 255° , is very slightly soluble in cold water, and not much more soluble in hot water, but dissolves in alcohol and ether.

Dry propylamine and carbon bisulphide likewise react immediately, with considerable development of heat. If the propylamine (2 mols.) is poured very gradually into the carbon bisulphide (1 mol.) and the mixture is cooled, a readily fusible solid mass is obtained, and if this is heated for about eight hours at 100 – 110° , hydrogen sulphide is evolved and symmetrical dipropylthiocarbamide is obtained. It is very slightly soluble in cold water, and somewhat more soluble in hot water, from which it crystallises in brilliant lamellæ resembling those of dipropylcarbamide. It melts at 68° , and dissolves readily in alcohol. Concentrated nitric acid completely oxidises dipropylthiocarbamide even at the ordinary temperature. C. H. B.

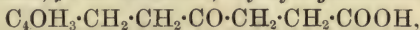
β -Furfurallevulinic acid; a New Synthesis of Cumarone Derivatives. By E. A. KEHRER and W. KLEBERG (*Ber.*, 26, 345–353).—The furfurallevulinic acid previously described by Ludwig and Kehler (*Abstr.*, 1891, 1456) is the δ -derivative and not the β -derivative, as has already been pointed out by Erdmann (*Abstr.*, 1892, 147). β -Furfurallevulinic acid, $C_4OH_3\cdot CH:CAc\cdot CH_2\cdot COOH$, may, however, be prepared by heating a mixture of levulinic acid, furfuraldehyde, and anhydrous sodium acetate in molecular proportion in a reflux apparatus. After purification, it crystallises from alcohol in yellow, strongly refractive prisms or tablets, and melts at 153° . It dissolves in concentrated sulphuric acid with a green colour, which on addition of water becomes first greenish-yellow, then yellow, and finally disappears. The calcium salt $(C_{10}H_9O_4)_2Ca + 2H_2O$, is a yellow, amorphous compound, and becomes anhydrous at 100° ; the phenylhydrazone, $C_{16}H_{16}N_2O_3$, crystallises in yellow, rhombic plates, and melts at 168° . As the corresponding β -benzallevalulinic acid, when heated, is converted into 3-aceto-1-naphthol with the loss of water, it appeared probable that the β -furfural compound would undergo a similar change with formation of a cumarone derivative, and the authors, therefore, distilled it carefully in a current of hydrogen or carbonic anhydride. The distillate is treated with alkali, and the solution after extraction with ether subjected to the action of a rapid current of carbonic anhydride. The white, flocculent compound, after reprecipitation from alkaline solution, melts at 190° , and has the composition $C_{10}H_8O_3$; it is therefore, in all probability, the expected 3-aceto-1-hydroxycumarone, its formation corresponding exactly with that of α -naphthol from phenylisocrotonic acid.

In the preparation of δ -furfurallevulinic acid, and also to a lesser extent in the preparation of the β -compound, a yellow, pulverulent substance is obtained, which Erdmann has suggested may be δ -furfuralangelicalactone. The authors find, however, that it is a mixture of furfurallevulinic acid with $\beta\delta$ -difurfurallevulinic acid,



The latter compound melts at 148° , and crystallises from benzene or alcohol in yellow or yellowish-green crystals and from hot water, in which it is very sparingly soluble, in very slender, yellow needles; it reduces Fehling's solution at the boiling point, but not in the cold. When even slight traces of the acid are dissolved in concentrated sulphuric acid, a beautiful, cornflower-blue solution is obtained, which, on careful addition of water, passes through different shades of violet and red to orange and yellow. The reverse series of changes may be observed by gradually adding sulphuric acid to a solution of the acid in absolute methyl or ethyl alcohol. The *calcium* salt, $(C_{15}H_{11}O_5)_2Ca + 3H_2O$, crystallises in bundles of needles, and becomes anhydrous at 100° ; the *silver* salt, $C_{15}H_{11}O_5Ag$, is an amorphous precipitate, unaffected by light.

All three acids when reduced with sodium amalgam, yield the corresponding furfuryl derivatives; *δ -furfuryllevalinic acid*,



crystallises in long, transparent needles melting at 98° ; *β -furfuryllevalinic acid* in white, granular crystals, or sometimes in needles or prisms melting at 100 – 101° , and *$\beta\delta$ -difurfuryllevalinic acid* in crystalline groups melting at 71 – 72° .

H. G. C.

Hydro-derivatives of Benzene. By A. BAEYER (*Ber.*, 26, 229–231). — Hexahydrobenzene is easily prepared by treating quinitol (*Abstr.*, 1892, 833) with hydriodic acid, and reducing the diiodide thus obtained with zinc dust and acetic acid. It is a very volatile oil, having an odour resembling that of petroleum, and is without action on permanganate.

The *iodhydrin of quinitol* is obtained by treating quinitol with dilute hydriodic acid, and is a colourless oil somewhat soluble in water. When treated with alkalis, it yields an oil which has a strong odour of capryl alcohol, is an unsaturated compound, and is probably a tetrahydrophenol.

Hexahydrophenol is easily prepared by reducing the iodhydrin with zinc dust and acetic acid. It boils at 157 – 159° under 720 mm. pressure, solidifies at a low temperature to a scaly mass, melts at 15° , has an odour resembling that of fusel oil, and is stable towards permanganate in the cold.

Bromhexahydrobenzene is obtained by heating the preceding alcohol with hydrobromic acid. It is a colourless oil, and boils at 162 – 163° under 714 mm. pressure.

Tetrahydrobenzene is obtained by distilling the preceding monobromide with quinoline. It boils at 82° , and yields a liquid dibromide and a nitrosochloride melting at 152 – 153° . The alcoholic solution turns yellow on addition of concentrated sulphuric acid.

The dihydrobenzene obtained from the dibromide of quinitol (*Abstr.*, 1892, 1074), when dissolved in alcoholic sulphuric acid, gives a blue solution having a characteristic absorption spectrum with two distinct bands in the yellow and green and a paler one in the blue. It will be of interest to determine if the blue solution of sylvestrene in alcoholic sulphuric acid shows a similar spectrum. Dihydrobenzene and tetrahydrobenzene are easily distinguished.

The former gives a crystalline tetrabromide, and a blue solution with alcoholic sulphuric acid; the latter a liquid dibromide and a yellow solution with alcoholic sulphuric acid.

When the dibromide of tetrahydrobenzene is distilled with quinoline, it yields only a trace of dihydrobenzene; this, however, gives the same absorption spectrum as the dihydrobenzene obtained from quinitol.

E. C. R.

Preparation of Orthodinitrobenzene. By C. A. LOBRY DE BRUYN (*Ber.*, **26**, 266—267).—The residue obtained in the preparation of metadinitrobenzene is heated with 2 parts of commercial nitric acid (sp. gr. 1.4) until the solution is almost colourless, the liquid is then poured into 5—6 parts of cold nitric acid and allowed to remain until the orthodinitrobenzene is deposited; it is then quickly collected, washed with nitric acid, and recrystallised from alcohol.

The author mentions a number of ortho-compounds which may be prepared from pure orthodinitrobenzene.

J. B. T.

Reaction of Phenyl Iododichloride and Iodosobenzene. By R. OTTO (*Ber.*, **26**, 305—306; compare this vol. i, 149).—Phenyl iododichloride and thiophenol, when mixed in chloroform solution, react energetically with evolution of hydrogen chloride, and yield iodobenzene and phenyl bisulphide.

Phenyl iododichloride and sodium benzenesulphinate, in a similar way, yield benzenesulphochloride and iodobenzene together with a small quantity of a compound melting at 180—190°.

Iodosobenzene reacts with thiophenol in the same way as phenyl iododichloride and yields iodobenzene and phenyl bisulphide.

E. C. R.

Aromatic Iododichlorides, Iodoso- and Iodoxy-compounds. By C. WILLGERODT (*Ber.*, **26**, 357—362; compare this vol., p. 149).—Phenyl iododichloride reacts with water at ordinary temperatures forming iodobenzene, hydrochloric acid, hypochlorous acid, and iodosobenzene; the latter compound may be separated by treating the solid product with nitric acid; iodosobenzene is oxidised on evaporating its aqueous solution, iodoxybenzene being formed; this explodes at 230° and at lower temperatures when impure. Iodosobenzene may also be prepared by the action of potash or soda on phenyl iododichloride.

Iodoxybenzene is readily obtained by heating iodosobenzene with water in a retort; iodobenzene volatilises with the steam, and the oxy-compound is deposited on cooling.

Paratolyl iododichloride, $C_6H_4Me \cdot ICl_2$, is prepared by the chlorination of pariodotoluene, and is deposited from chloroform in needles which decompose at 85°, whilst from carbon tetrachloride granular, rhombic crystals are formed which explode at 100—118°; with alcohol, it reacts like the corresponding benzene compound.

Pariodosotoluene, $C_6H_4Me \cdot IO$, is obtained by the action of soda on the preceding compound, and is purified by treatment with chloroform, which removes iodotoluene; it closely resembles the corresponding

benzene derivative, softens at 130° , and melts, with evolution of gas, at about $175-178^{\circ}$. The *acetate* and *nitrate* are crystalline; the latter decomposes without explosion at $90-92^{\circ}$.

Pariodoxytoluene, $C_6H_4Me \cdot IO_2$, is prepared in a similar manner to the benzene derivative, and explodes at 228° .

Orthotolyl iododichloride is more readily soluble than the para-compound, and decomposes at about 91° with previous softening.

Orthiodosotoluene is almost colourless, and decomposes at 178° .

Orthiodoxytoluene is crystalline, and explodes at 210° .

Parabromiodosobenzene, $C_6H_4Br \cdot IO$, is a pale yellow, amorphous compound, decomposing at 185° . The *acetate* and *nitrate* are crystalline; the latter melts at $96-97^{\circ}$ with decomposition.

Parabromiodoxybenzene, $C_6H_4Br \cdot IO_2$, crystallises from glacial acetic acid in colourless plates, and explodes at 240° . *Paranitroiodosobenzene*, $NO_2 \cdot C_6H_4 \cdot IO$, is prepared from paranitrophenyl iododichloride, and decomposes at 78° .
J. B. T.

Titanium Compounds. By L. LEVY (*Ann. Chim. Phys.* [6], **25**, 433—519).—Most of the work recorded in this paper has been published elsewhere in the course of the last five years (compare *Abstr.*, 1888, 27, 196, 423, 1254; 1889, 572; and 1890, 1066); the following compounds seem not to have been described before.

Phenyl titanate, $Ti(OPh)_4$, prepared by treating titanium tetrachloride with phenol in benzene solution, is a red, crystalline substance, which decomposes at 100° , and melts at about 143° when quickly heated. It is decomposed by nascent hydrogen, yields dichlorophenol on treatment with chlorine, and is converted into tribromophenol and titanium tetrabromide when submitted to the action of bromine vapour; with iodine, it gives iodophenol and titanium tetriodide. It is decomposed by water and by dilute alcohol, yielding phenol and a yellow substance; it dissolves in concentrated mineral acids, and is readily decomposed by alkalis.

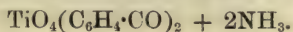
A compound of the composition $2TiCl_4, Ti[O \cdot C_6H_2(NO_2)_3]_4$ is obtained when titanium tetrachloride is treated with picric acid in benzene solution; it is a brick-red, crystalline substance, and is decomposed by water; on prolonged boiling with benzene, it is decomposed into *picric titanate*, $Ti[O \cdot C_6H_2(NO_2)_3]_4$.

Paracresyl titanate, $Ti(O \cdot C_7H_7)_4$, is a reddish-brown, crystalline, deliquescent substance; the corresponding *meta*-compound is deliquescent and unstable.

Thymol titanate, $Ti(O \cdot C_{10}H_{13})_4$, is a crystalline, very deliquescent substance, readily soluble in most ordinary solvents.

α -*Naphthyl titanate*, $Ti(O \cdot C_{10}H_7)_4$, is a brown, amorphous substance insoluble in neutral liquids; the corresponding β -compound was not obtained in a pure condition.

A red, crystalline compound of the composition $TiO_4(C_6H_4 \cdot CO)_2$ is obtained when salicylic acid is treated with titanium tetrachloride in benzene solution; it is decomposed by water, and combines with ammonia, yielding a yellow substance of the composition



F. S. K.

Synthesis of a Dihydrocymene. By A. BAEYER (*Ber.*, 26, 232—234).—The following ethyl dialkylsuccinosuccinates are prepared as formerly described (*Abstr.*, 1892, 1182):—

Ethyl diethylsuccinosuccinate boils at 215° under 15 mm. pressure. The *trans*-compound melts at 65—66°, the *cis*-compound is an oil.

Ethyl dipropylsuccinosuccinate boils at 217—218° under 15 mm. pressure. The *trans*-compound melts at 86—87°; the *cis*-compound is an oil.

Ethyl diisopropylsuccinosuccinate boils at 215—220° under 15 mm. pressure. The *trans*-compound melts at 116—117°; the *cis*-compound is an oil.

From these ethereal salts, the dialkyl diketones are obtained by hydrolysis with dilute sulphuric acid, and by reduction with sodium are converted into the corresponding quinitols. The latter yield dibromides, which, when boiled with quinoline, are converted into dihydro-derivatives of the homologues of benzene. Thus the diethyl compound yields the following:—The *diethyl diketone* in the *trans*-modification melts at 49—50°, in the *cis*-modification at 12°. The *quinitol* is a syrup. The *bromides* are oils. The *dihydrodiethylbenzene* boils at 180—185° (uncorr.), and has a terpene-like odour.

Monalkyl compounds are obtained by heating a mixture of ethyl succinosuccinate and the sodium compound of the same with an alkyl iodide. They are all liquids, dissolve in dilute alkalis without decomposition, and yield diketones, quinitols, and dihydrobenzenes containing one alkyl group. The *methyl* compound boils at 181—182° under 15 mm. pressure; the *propyl* and *isopropyl* compounds boil at about 200°.

Methyl propyl compounds are obtained by heating sodium ethoxide, methyl iodide, and ethyl propylsuccinosuccinate dissolved in benzene for 4—5 hours at 100°.

Ethyl methylpropylsuccinosuccinate is a colourless oil, boils at 195—200° under 15 mm. pressure, and yields a diketone melting at 80°.

Ethyl methylisopropylsuccinosuccinate is a colourless oil, boils at 195—200° under 15 mm. pressure, and yields a diketone, of which the *trans*-modification melts at 64—65°. The quinitol and dibromide are oils. The latter yields

Methylisopropyldihydrobenzene, or *dihydrocymene*, when heated with quinoline. Dihydrocymene boils at 174° (corr.), has a faint odour of turpentine, quickly resinifies on exposure to air, instantaneously decolorises permanganate, and unites with bromine like a terpene. Owing to the small quantity of material, the author was unable to determine if the dihydrocymene is terpinene or an unknown terpene, but it undoubtedly belongs to the class of terpenes, and he considers that the problem of the artificial preparation of a turpentine oil from the simple compounds—acetic acid or acetone or succinic acid—is solved.

E. C. R.

Ethers of Homocatechol. By H. COUSIN (*Compt. rend.*, 116, 104—106).—The mono- and di-methyl and mono- and di-ethyl ethers of homocatechol are obtained in the usual way by the action of the

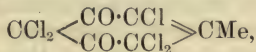
corresponding alkyl iodide on homocatechol in presence of a solution of potassium hydroxide in the corresponding alcohol. The *monomethyl ether* is a colourless liquid, with a strong odour of creosote; it boils at 217—220°, and is insoluble in water, but dissolves in alcohol, ether, and solutions of alkalis; sp. gr. at 0° = 1.1106. The sp. gr. of creosol at 0° is 1.0971, and it boils at 218—219°. The compound solidifies on contact with concentrated alcoholic potash, like the creosol from creosote. The *dimethyl ether* has similar properties, but is insoluble in solutions of alkalis, and boils at 216—217°; sp. gr. at 0° = 1.0668.

The *monethyl ether* boils with partial decomposition at 226—227° under ordinary pressure; sp. gr. at 0° = 1.0928. It is very soluble in water, alcohol, ether, and concentrated solutions of alkalis, but does not solidify in contact with concentrated alcoholic potash. Its aqueous solution gives, with ferric chloride, a green coloration which rapidly changes to brown. The *diethyl ether* is likewise a colourless liquid, with an odour of creosote; it boils at 228°, with partial decomposition; sp. gr. at 0° = 1.0303. It is very soluble in water, and the solution gives no coloration with ferric chloride; it dissolves in alcohol and ether, but is insoluble in solutions of alkalis. The *methyl ethyl ether*, previously described by Hlasiwetz, boils at 223—224°; sp. gr. at 0° = 1.032.

The *diacetyl derivative*, $C_6H_3Me(OAc)_2$ [Me : OAc : OAc = 1 : 3 : 4], is obtained by the action of acetic anhydride on homocatechol. It is a viscous liquid which becomes yellow when exposed to light; it boils at 160—161° under a pressure of 70 mm., and at 263—264° with partial decomposition under ordinary pressure. It is only slightly soluble in water, and the solution gives no coloration with ferric chloride; it dissolves in alcohol and ether, and is decomposed by alkalis, even in dilute solution. Alcoholic potash yields ethyl acetate.

C. H. B.

Action of Chlorine on Phenols. By T. ZINCKE (*Ber.*, 26, 311—324).—*The Action of Chlorine on Orcinol.*—The action of chlorine on orcinol is very similar to its action on resorcinol (*Abstr.*, 1891, 689), the first product is a trichlororocinol $C_6MeCl_3(OH)_2$, which, by the further action of chlorine, is converted into pentachlororocinol (1 : 3 : 5-diketomethylpentachlorohexamethylene),



obtained by Stenhouse by the action of hydrochloric acid and potassium chlorate on orcinol. It crystallises in large, transparent prisms, and melts at 120.5°. When boiled with alcohol, it is decomposed, and yields an oily compound. When treated, in a finely-divided state, with water, it is slowly converted into a hydrate, and then into dichloroacetyltrichloromethylcrotonic acid, $CHCl_2 \cdot CO \cdot CCl : CMe \cdot CCl_2 \cdot COOH$; the same acid is more easily obtained by employing a solution of sodium acetate and then precipitating with concentrated hydrochloric acid. When the pentachloro-compound is boiled with water, the same acid is obtained, but at once decomposes, and yields a mixture

of ketones. When heated with phosphorus pentachloride at 230° , it yields hexachlorobenzene and heptachlorotoluene (m. p. 119.5°). The latter is identical with the compound prepared by Beilstein and Kuhlberg (*Annalen*, **150**, 306), although they state that it melts at 109° .

Trichlororcinol is very easily obtained by reducing the pentachloro-compound with stannous chloride. It crystallises from water or dilute acetic acid in slender, white needles containing $2\frac{1}{2}$ mols. H_2O , from benzene in transparent cubes containing benzene, and from glacial acetic acid in crystals containing acetic acid. When dry, it melts at 127° , and not at 123° , as stated by Stenhouse. The *acetyl compound* crystallises in white needles, and melts at 130 — 131° .

Dichloracetyltrichloromethylcrotonic acid, prepared as stated above, crystallises in large, transparent prisms, melts at 115° , and is easily decomposed by the action of bases, and by heating with water. The *methyl salt* crystallises in thick, colourless needles or prisms, and melts at 113° . The *amide*, obtained by treating pentachlororcinol dissolved in benzene with dry ammonia, crystallises in white needles, melts at 175° , has feeble acid properties, and dissolves in sodium carbonate. When the acid is decomposed by water in a distillation flask, the product distils over as an oil which boils at 150 — 160° under 23 mm. pressure, and is a mixture of the ketones $C_6H_5Cl_5O$ and $C_6H_5Cl_3O_2$. These compounds resemble the crude ketones obtained from pentachlororesorcinol, but could not be characterised, nor do they yield compounds with orthophenylenediamine.

When the acid is decomposed by sodium carbonate, it yields a neutral compound and an acid which, on warming, evolves hydrogen chloride and carbonic anhydride, and is converted into *methyldichlorometadiketopentene*, $C_5HMeCl_2O_2$. The latter crystallises in white, lustrous leaflets, melts at 80° , and is easily volatile with steam. The neutral compound has the formula $C_6H_3Cl_3O$, crystallises in colourless prisms, melts at 182 — 183° , and is identical with the compound obtained by Bergmann from the orthodiketo-chloride $C_6MeCl_3O_2$ (*Inaug. Dissert.*, Marburg, 1892).

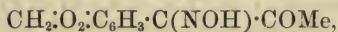
Trichloracetyltrichloromethylcrotonic acid,



is obtained by the action of bleaching powder on pentachlororcinol, and also by the action of bleaching powder and acetic or hydrochloric acid on orcinol. Stenhouse erroneously states that when acetic acid is employed, the product is an acid of the composition $C_6H_4Cl_4O_3$, which melts at 130° (*Ber.*, **6**, 575). It crystallises in colourless prisms, melts at 140.5° , and, when strongly heated, decomposes with evolution of carbonic anhydride and hydrogen chloride. When distilled with steam, it yields an oily ketone of the composition C_5Cl_5MeO , which yields chloroform when treated with alkalis. When treated with excess of alkali, it yields chloroform and an acid which has not yet been isolated. When dissolved in sodium acetate and treated with ammonia, it yields a compound of the formula C_5HMeCl_2NO , which crystallises in slender, white needles, melts at 187.5° , is a weak

acid, and yields a sodium salt which crystallises in lustrous leaflets, and is decomposed by water. E. C. R.

Action of Nitrous acid on Isosafrole. By A. ANGELI (*Gazzetta*, 22, ii, 445—492; compare this vol., i, 196).—Isosafrole nitrosite dissolves in alcoholic potash with development of heat, and, on pouring the product into water and acidifying, *isonitrosoisosafrole*,

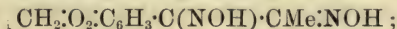


separates; when purified, it forms lustrous, yellow scales, and melts at 98° . On treatment with hydroxylamine hydrochloride, this substance yields a compound of the composition $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_7$, which crystallises in silvery scales melting at 112° ; it is soluble in boiling alcohol, benzene, or ethyl acetate, but insoluble in water or light petroleum. The reaction by which it is formed is probably similar to the reaction between hydroxylamine and isonitrosoacetophenone (Scholl, Abstr., 1891, 287) or phenylglyoxal (Müller and v. Pechmann, Abstr., 1890, 51).

Isosafrolenitrolpiperidide, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{C}(\text{NOH})\cdot\text{CHMe}\cdot\text{C}_5\text{NH}_{10}$, is prepared by heating the nitrosite with excess of piperidine in alcoholic solution, the liquid is poured into water, and the precipitate crystallised from alcohol; it is thus obtained in white scales melting at 134° . It is soluble in most solvents and acids, has somewhat pronounced basic properties, and gives a *picrate* which crystallises in yellow needles.

Diisonitrosoisosafrole peroxide gives a normal molecular weight by the cryoscopic method in benzene solution. It is very stable towards acids, being precipitated, unaltered, from its sulphuric acid solution by water, and is but little attacked on heating in a sealed tube with hydrochloric acid at 150° ; at higher temperatures carbonisation occurs. It is not acted on by acetic anhydride at 210° . Alkaline permanganate oxidises the peroxide with formation of piperonylic acid, and with nitric acid it yields a *nitro*-derivative, $\text{NO}_2\cdot\text{C}_{10}\text{H}_7\text{N}_2\text{O}_4$; this crystallises in yellowish needles melting at 144° , and gives nitro-piperonylic acid on oxidation with alkaline permanganate. The peroxide yields a *monobromo*-derivative which forms long, white needles melting at 115° .

On reducing diisonitrosoisosafrole peroxide with zinc dust in acetic acid solution, a substance, crystallising in white needles and melting at 210° , is obtained, together with α -diisonitrosoisosafrole,



the latter forms lustrous, colourless prisms, and melts at 159° . It is very soluble in alcohol or ethyl acetate, sparingly so in benzene, and is precipitated by carbonic anhydride from its solution in alkalis; it yields a *diacetyl* derivative, $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_4\text{Ac}_2$, which forms large, white scales melting at 138° , and slowly decomposes in alcoholic solution. α -Diisonitrosoisosafrole is readily oxidised by alkaline ferricyanide solution, yielding the peroxide from which it was obtained.

The facility with which glyoximes yield peroxides on oxidation has been pointed out by Scholl (Abstr., 1891, 315) and others, but the reduction of a peroxide to the corresponding glyoxime described above is the first case of the kind recorded. The author has also succeeded in reducing diphenylglyoxime peroxide to γ -benziledioxime, a reaction which Auwers and V. Meyer failed to effect (Abstr., 1888, 597).

β -*Diisonitrosoisosafrole*, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:C(NO H)\cdot CMe\cdot NOH}$, is obtained by heating α -diisonitrosoisosafrole for an hour at 159° . It forms lustrous, colourless prisms, melts at 209° with decomposition, and is sparingly soluble in alcohol. It yields the same diacetyl derivative as its α -isomeride, and gives the same peroxide on oxidation with ferricyanide. The β -dioxime is also obtained by the action of nitrous acid on the α -compound.

Homoacetopiperone, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH}_2\text{:COMe}$, is obtained by reducing the peroxide with zinc dust (Abstr., 1892, 1198); it forms almost colourless needles, melts at 38° , and is very soluble in most solvents, but only sparingly so in light petroleum. It yields a *hydrazone*, $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$, which crystallises in yellow needles melting at 97° , and resinifies on exposure to the air. The reduction with zinc dust also yields a *substance* $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_4$, which forms large, white needles melting at 180° ; this gives a normal molecular weight by the cryoscopic method in benzene solution, but its constitution is uncertain. It behaves as a feeble base, and gives a violet colour with concentrated sulphuric acid.

Diisonitrosoisosafrole anhydride, $\text{O} \begin{array}{c} \text{N:C}\cdot\text{C}_6\text{H}_3\text{:O}_2\text{:CH}_2 \\ \text{N:CMe} \end{array}$, is obtained on reducing the peroxide with phosphorus sulphide, or tin and hydrochloric acid; it forms highly refractive, lustrous crystals, melts at 86° , and has a normal molecular weight in freezing benzene. It is soluble in benzene, ethyl acetate, or acetone, sparingly so in alcohol, and dissolves without decomposition in concentrated sulphuric acid.

Alcoholic potash converts the peroxide into an *isomeride*, $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_4$, which forms microscopic, acicular aggregates melting at 185° with decomposition; it soon turns red in the air, and is soluble in alcohol, acetone, or ethyl acetate, sparingly so in light petroleum. It dissolves readily in alkalis, and separates on acidification; dilute acids convert it into piperonylnitrile, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CN}$. It does not combine with bromine in the cold, and gives a resinous product with phosphorus pentachloride. The *acetyl* derivative, $\text{C}_{10}\text{H}_7\text{N}_2\text{O}_4\text{Ac}$, which forms almost colourless, lustrous laminae melting at 129° , is more stable than the parent substance, although it gives the normal molecular weight by the cryoscopic method in acetic acid solution. The *benzoyl* derivative, $\text{C}_{10}\text{H}_7\text{N}_2\text{O}_4\text{Bz}$, forms small, very hard, lustrous crystals melting at 146° with decomposition. With phenylhydrazine, a *substance*, $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_2$, is obtained which possibly has the constitution $\text{C}_{10}\text{H}_7\text{O}_2(\text{N}_2\text{Ph})\cdot\text{N}_2\text{HPh}$; it forms yellow needles melting at about 168° . As the isomeride of the peroxide is readily oxidised by alkaline permanganate with formation of piperonylnitrile, its constitution is probably $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:C} \begin{array}{c} \text{CO}\cdot\text{CH}_2 \\ \text{N}-\text{O} \end{array}$.

Isosafrole yields a *nitrosochloride*, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{C}_3\text{H}_5\cdot\text{NOCl}$, which is obtained as a white, crystalline powder melting at 132° .

W. J. P.

Action of Nitrous acid on Isoapiole. By A. ANGELI and P. BARTOLOTTI (*Gazzetta*, 22, 493—509).—The action of nitrous acid on isoapiole is, in all respects, analogous to its action on isosafrole (compare preceding abstract).

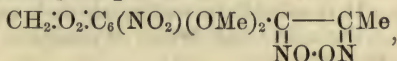
Diisonitrosoisoapiole peroxide, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}(\text{OMe})_2\cdot\overset{\text{O}}{\underset{\text{NO}\cdot\text{ON}}{\text{C}}}\text{---}\overset{\text{O}}{\underset{\text{NO}\cdot\text{ON}}{\text{C}}}\text{Me}$, is obtained by dissolving isoapiole in acetic acid and adding potassium nitrite solution; much heat is developed, and the peroxide is deposited. When pure, it forms minute, yellow needles, melting at $169\text{--}170^\circ$. Like the corresponding isosafrole derivative, it is converted by alcoholic potash into an *isomeride*, probably having the constitution $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}(\text{OMe})_2\cdot\overset{\text{O}}{\underset{\text{N}}{\text{C}}}\text{---}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{C}(\text{NOH})\cdot\text{CH}_2$, which forms almost colourless needles, melting at $168\text{--}170^\circ$ with decomposition.

Diisonitrosoisoapiole anhydride, $\text{O} < \overset{\text{N}}{\underset{\text{N}}{\text{C}}}\cdot\text{C}_6\text{H}(\text{OMe})_2\cdot\text{O}_2\cdot\text{CH}_2$, obtained by reducing the peroxide with tin and hydrochloric acid, crystallises in white needles, and melts at 138° .

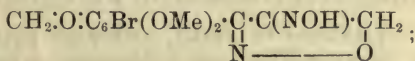
On oxidation with alkaline permanganate, the peroxide yields an *acid* which forms lustrous, micaceous scales melting at 61° and containing nitrogen. Its composition could not be determined, owing to the small quantity obtained; a solution of its ammonium salt gives a white precipitate with salts of lead, barium, or calcium. The same acid is formed on oxidising diisonitrosoisoapiole.

α -Diisonitrosoisoapiole, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}(\text{OMe})_2\cdot\overset{\text{O}}{\underset{\text{NOH}}{\text{C}}}\text{---}\overset{\text{O}}{\underset{\text{NOH}}{\text{C}}}\text{Me}\cdot\text{NOH}$, prepared by reducing the peroxide with zinc-dust and acetic acid, forms colourless crystals melting at 154° ; on oxidation with alkaline ferricyanide solution, it yields the peroxide from which it was derived. The *diacetyl* derivative, $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_6\text{Ac}_2$, forms beautiful, yellow crystals melting at $137\text{--}138^\circ$. The α -dioxime is converted, by heating at a few degrees above its melting point, into the isomeric *β -diisonitrosoisoapiole*; this is much less soluble in alcohol than the α -compound, and forms lustrous, colourless crystals melting at $197\text{--}198^\circ$.

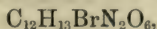
Diisonitrosoisoapiole peroxide,



is obtained by the action of nitric acid on the peroxide described above; it forms lustrous, yellow needles melting at $122\text{--}123^\circ$. The corresponding *bromo*-compound, $\text{C}_{12}\text{H}_{11}\text{BrN}_2\text{O}_6$, is prepared by the action of bromine on diisonitrosoisoapiole peroxide; it is obtained in minute, yellow needles melting at 131° . Like the parent peroxide, it is converted by alcoholic potash into an *isomeride*,



this substance forms small, almost colourless crystals, melting at 127—128°. On reduction with zinc-dust and acetic acid, the bromo-derivative of the peroxide yields *diisonitrosobromoisopiole*,



in brilliant crystals, which turn brown at 182° and melt at 220°. An *isomeride* of this substance is obtained on dissolving it in acetic anhydride and precipitating the solution with an alkali; it forms white crystals melting at 94—95°. W. J. P.

Compounds of Malic and Fumaric acids with Aromatic Amines. By E. GIUSTINIANI (*L'Orosi*, 1892, 361—375, and *Gazzetta*, 23, i, 168—184; compare Abstr., 1892, 820).—Benzylfumarimide crystallises in the anorthic system, $a : b : c = ?$, $\alpha = 85^\circ 54'$, $\beta = 70^\circ 14'$, $\gamma = 80^\circ 44'$, and on reduction with zinc-dust gives a substance of pyrrolic nature. α -Benzylmalimide is obtained in square, monosymmetric laminae, $a : b : c = 1 : ? : 1.23$, $\beta = 69^\circ 17'$, whilst β -benzylmalimide forms orthorhombic prisms, $a : b : c = 0.5865 : 1 : 0.2253$. The specific rotatory power of both isomerides in aqueous solution varies greatly with the concentration; in a 2.28 per cent. solution, the former gives $[\alpha]_D = -23.28^\circ$, whilst a 2.255 per cent. solution of the β -isomeride has $[\alpha]_D = -48.56^\circ$. Benzylmalamic acid, obtained from either imide, is slightly lævorotatory.

Aniline hydrogen malate forms small, white crystals melting at about 135°. On heating it at 150—160°, water is evolved, and a substance melting at 190° is obtained, together with malanilide and malanil; at about 200°, the latter loses water, and gives a mixture of fumaric acid and fumaranilide. Malanil is lævorotatory; $[\alpha]_D = -34.12^\circ$ in a 0.2244 per cent. aqueous solution.

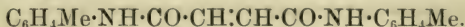
Paratoluidine hydrogen malate loses water at 150°, giving *paratolyimide*, $\begin{array}{c} \text{CH(OH)} \cdot \text{CO} \\ | \\ \text{CH}_2 - \text{CO} \end{array} > \text{N} \cdot \text{C}_6\text{H}_4\text{Me}$, and *paratolylmalamide*,



The imide forms minute, yellowish crystals, melts at 184°, and is very soluble in alcohol, ether, or chloroform, less so in water or benzene. On treatment with an alkali, it yields *paratolylmalamic acid*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH(OH)} \cdot \text{CH}_2 \cdot \text{COOH}$, which crystallises in thin, iridescent laminae. It is soluble in water, alcohol, or ether, and gives very soluble salts. The *silver* salt forms crystalline granules, which are sensitive to light.

Paratolylmalamide is obtained in white needles melting at 195°; it is soluble in alcohol, sparingly so in water or ether, and on treatment with concentrated alkalis yields paratoluidine.

On heating paratoluidine hydrogen malate at above 200°, water and paratoluidine distil, together with *paratolylfumaramide*,



This substance crystallises in small, yellowish pyramids, melts at 142°, and yields paratoluidine and a fumarate when treated with

alkalis. The *dibromide*, $C_{18}H_{18}N_2O_2Br_2$, forms crystalline granules melting at 168° with decomposition.

Orthotoluidine hydrogen malate is converted into *orthotolylmalamide*, $C_{18}H_{20}N_2O_2$, at 140° ; this separates from alcohol in slightly coloured laminæ melting at 179° ; it is very soluble in alcohol or ether, sparingly so in water, and yields orthotoluidine with concentrated alkalis. On heating the malate at 200 – 220° , an oily distillate is obtained, which probably contains *orthotolylfumaramide*. The *dibromide* forms a crystalline powder which blackens at 200° .

W. J. P.

Action of Carbamide on Nitrosamines. By J. TAFEL and I. VOGEL (*Ber.*, **26**, 335–337).—The regeneration of the original bases from the nitrosamines can usually be brought about by the action of concentrated hydrochloric acid, or by treatment with strong reducing agents, such as tin and hydrochloric acid. In the case of certain tetrahydroquinoline derivatives, the authors find that both these methods cause very great loss of substance, and that a much better yield can be obtained by heating the nitrosamines with carbamide. The reaction corresponds exactly with that of carbamide on nitrous acid, nitrogen and carbonic anhydride being liberated. To carry out the reaction, the nitrosamine is heated with twice the theoretical quantity of carbamide in a distilling flask, the temperature being raised, as the evolution of nitrogen slackens, until it has reached 190 – 200° ; the melt is extracted with warm water, acidified, filtered, and separated from unaltered nitrosamine by extraction with ether or distillation with steam; the residue is then saturated with alkali, and the base isolated in the usual manner.

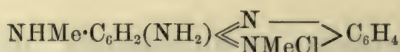
H. G. C.

Paramidoalkylorthotoluidine. By A. WEINBERG (*Ber.*, **26**, 307–308).—An answer to the criticisms of Rosenstiehl (*Abstr.*, 1892, 1319) and Bernthsen (this vol., i, 75) on the author's previous results (*Abstr.*, 1892, 1078).

Metamidophenol and its Derivatives. By M. IKUTA (*Amer. Chem. J.*, **15**, 39–44).—Leonhardt's method of making metamidophenol (D. R. P., 49,060) consists in heating resorcinol with ammonium chloride and aqueous ammonia for 10 hours at 200° . The hydrochloride is thus formed, and after the excess of resorcinol has been removed by treatment with ether, the free base is separated in the usual way and recrystallised from toluene. Metamidophenol crystallises in colourless prisms, melts at 122 – 123° , and is perfectly stable. In alkaline solution, however, it suffers partial decomposition. The *haloid salts* and *acid sulphate* are crystalline and stable, subliming with partial decomposition. The *monacetyl derivative* (*metahydroxyacetanilide*) crystallises in colourless needles, and melts at 148 – 149° . The *diacetyl derivative*, $OAc \cdot C_6H_4 \cdot NHAc$, crystallises in colourless scales, and melts at 101° . The *monobenzoyl derivative* (*metahydroxybenzanilide*) crystallises in colourless, silky needles, and melts at 174° . The *dibenzoyl derivative*, $OBz \cdot C_6H_4 \cdot NHBz$, crys-

tallises in colourless scales, and melts at 153° . The *tribromo-derivative*, $\text{OH}\cdot\text{C}_6\text{HBr}_3\cdot\text{NH}_2$, crystallises in long, bright needles, and melts at 121° . It does not form salts with acids. JN. W.

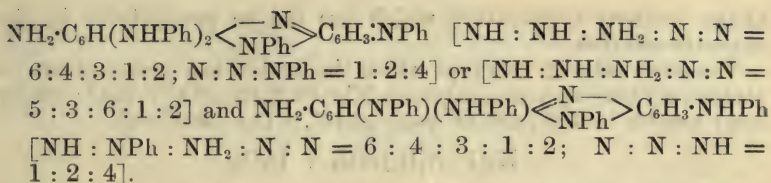
Oxidation Products of Orthodiamines. By O. FISCHER and O. HEILER (*Ber.*, **26**, 378—386; compare Kehrman and Messinger. (*J. pr. Chem.*, **46**, 566).—By the oxidation of methylorthophenylenediamine with ferric chloride in alcoholic solution, the hydrochloride of the azonium base is obtained, which has the formula



$[\text{NH}:\text{NH}_2:\text{N}:\text{N} = 5:4:1:2; \text{N}:\text{N} = 1:2]$; it crystallises from alcohol, with 2 mols. H_2O , in needles of metallic lustre, has strongly marked basic properties, and gives a red coloration with concentrated sulphuric acid. The *free base*, $\text{C}_{28}\text{H}_{30}\text{N}_8\text{O}$, is prepared from the preceding compound by the action of potash, and forms an unstable, red powder.

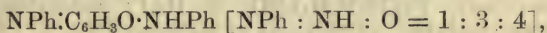
Anilidobenzeneinduline, $\text{NHPh}\cdot\text{C}_6\text{H}_2(\text{NH})\llangle\overset{\text{N}}{\text{NPh}}\rangle\text{C}_6\text{H}_4$, obtained by treating orthamidophenylamine with ferric chloride, crystallises from benzene in brownish-red plates, which remain unmelted below 240° ; with concentrated sulphuric acid, a violet-red coloration is obtained, with alcohol, a brown one. The *hydrochloride* is deposited in cantharidine-green plates. The formation of this substance is analogous to that of diamidophenazine from orthophenylenediamine. By the action of dilute sulphuric acid at 150 — 160° for three hours, it is converted into *anilidobenzeneindone*, $\text{NHPh}\cdot\text{C}_6\text{H}_2\text{O}\llangle\overset{\text{N}}{\text{NPh}}\rangle\text{C}_6\text{H}_4$, $[\text{O}=4]$; this crystallises from benzene in brown needles, and gives a green coloration with sulphuric acid, which changes to red on dilution. On heating the induline for six hours with sulphuric acid, *hydroxybenzeneindone*, $\text{HO}\cdot\text{C}_6\text{H}_2\text{O}\llangle\overset{\text{N}}{\text{NPh}}\rangle\text{C}_6\text{H}_4$, is formed; it is purified by solution in soda, and crystallises from alcohol in slender, lustrous, orange-red needles. Orthamidophenylamine, on distillation with 10 parts of lead oxide, yields phenazine. The amide from paramidodiphenylmetaphenylenediamine may be regarded either as anilidorthamidophenylamine, $\text{C}_6\text{H}_3(\text{NHPh})_2\cdot\text{NH}_2$ $[\text{NH}:\text{NH}:\text{NH}_2 = 1:3:4]$, or as a paradiamine. On oxidation with lead peroxide, it is converted into an *anilidophenylquinonediimide*, $\text{NH}\cdot\text{C}_6\text{H}_3(\text{NPh})\cdot\text{NHPh}$ $[\text{NPh}=1]$, which crystallises from light petroleum in orange-red, concentric needles and melts at 98° .

By the action of acids on the diimide in alcoholic solution, or of ferric chloride on the diamine, an induline derivative is obtained, which is deposited from benzene in lustrous, bronze-coloured prisms melting at 235° ; the base has well marked tinctorial powers, dissolves in alcohol with a blue colour, and gives a violet-red coloration with concentrated sulphuric acid. This compound is probably represented by one of the following formulæ:—



The *nitrate* and *sulphate* are sparingly soluble.

By the action of nitrous acid on paramidodiphenylmetaphenylenediamine, *anilidoquinonephenylimide*,



is obtained, anilidoquinonephenyldiimide being probably first formed; the phenylenediamine, therefore, reacts as a paradiamine. The compound is deposited from light petroleum in brick-red crystals melting at 125°; with sulphuric acid, a green coloration is obtained, which changes to violet on dilution; with glacial acetic acid, a blue dye is formed.

J. B. T.

Products of the Reduction of Orthophenylenediacetonitrile.

By C. U. ZANETTI (*Gazzetta*, **22**, ii, 510—514).—On reducing a boiling solution of orthophenylenediacetonitrile in absolute alcohol with metallic sodium, two bases are formed which may be separated by taking advantage of the different solubilities of their oxalates in water. The more soluble *oxalate* obtained is probably that of *orthophenylenediethyldiamine*, $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)_2$; the base is an oil, and yields a *picrate* which crystallises in yellow needles melting at 210° with previous decomposition. The *hydrochloride* is deliquescent and very soluble in alcohol.

The second base formed is probably the *imido*-compound, $\text{C}_{10}\text{H}_{13}\text{N}$, corresponding with the above amine; the preparation of such a base is of interest, as it is the type of a new series of closed chain compounds. Its *oxalate* forms small, white needles melting at 216—220° with decomposition, and is sparingly soluble in water. The *benzoyl* derivative separates from boiling alcohol in flat, white needles, and melts at 150—152°.

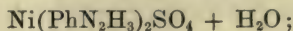
The author is continuing the investigation.

W. J. P.

Compounds of Phenylhydrazine with Metallic Salts. By H. SCHJEERNING (*J. pr. Chem.* [2], **47**, 80—88; see also *Abstr.*, 1892, 1454).—*Zinc phenylhydrazine sulphate*, $\text{Zn}(\text{PhN}_2\text{H}_3)_2\text{SO}_4 + \text{H}_2\text{O}$, crystallises from a hot concentrated mixture of zinc sulphate solution with phenylhydrazine. It is colourless or very pale yellow, but becomes reddish in air by oxidation of the phenylhydrazine. One part of the salt dissolves in 185 parts of water at 19·5°. At 105°, it loses its water of crystallisation; at 170°, it loses phenylhydrazine; above 170°, in a test tube, it explodes slightly. Its reactions are those of both zinc sulphate and phenylhydrazine; a solution of it serves to precipitate certain proteïds

at the ordinary temperature, which are not so precipitated by zinc sulphate solution.

The other salts of this type which the author has prepared are :—*Cadmium phenylhydrazine sulphate*, $5\text{Cd}(\text{PhN}_2\text{H}_3)_2\text{SO}_4 + \text{H}_2\text{O}$; colourless; soluble in 312 parts of water at 17° . The *nickel salt*,



bright green; soluble in 862 parts of water at 17° . The *cobalt salt*, $\text{Co}(\text{PhN}_2\text{H}_3)_2\text{SO}_4 + \text{H}_2\text{O}$; bright red; soluble in 270 parts of water at 17° . The *manganous salt*, $\text{Mn}(\text{PhN}_2\text{H}_3)_2\text{SO}_4 + \text{H}_2\text{O}$; colourless or pale yellow; very unstable in air; soluble in 55 parts of water at 16° . The *ferrous salt*, $\text{Fe}(\text{PhN}_2\text{H}_3)_2\text{SO}_4 + \text{H}_2\text{O}$; colourless; rapidly oxidises in air; soluble in 240 parts of water at 18° . A. G. B.

Preparation of Methylbenzoïc Anilide. By J. DUPONT (*Bull. Soc. Chim.* [3], 7, 516).—Benzoïc anilide cannot be methylated by Pictet's method (Abstr., 1888, 364). A. R. L.

Orthocyanobenzoïc acid. By S. HOOGEWERFF and W. A. VAN DORP (*Rec. Trav. Chim.*, 11, 84—102).—The formation of orthocyanobenzoïc acid from phthalic chloride and ammonia is probably preceded by that of an intermediate compound, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{C}(\text{NH}) \\ \text{CO} \end{smallmatrix}\rangle\text{O}$. The melting point of the acid given by Auger (Abstr., 1888, 953) is too low; the author finds that the acid melts between 180° and 190° , passing, with resolidification, into phthalimide, which then melts at about 230° (compare Allendorf, Abstr., 1891, 1370). The *ammonium salt* forms needles, melts at 160 — 170° with the evolution of gas, then resolidifies, and again melts at 220 — 230° ; the *methyl salt* crystallises in flat needles, is sparingly soluble in cold water, and melts at 50 — 51° , whilst the *ethyl salt* melts at 65 — 66° (not 70° ; see Müller, Abstr., 1886, 803). Phthalamic acid is formed when orthocyanobenzoïc acid is dissolved in concentrated sulphuric acid. The *compound* $\text{S}[\text{C}(\text{NH})\cdot\text{C}_6\text{H}_4\cdot\text{COONH}_4]_2$ is obtained by treating orthocyanobenzoïc acid with alcoholic ammonium sulphide; it melts at 145° . The formation of the latter compound is analogous to that of thio-benzamide from benzonitrile and ammonium sulphide, and therefore furnishes another argument in favour of the view that the compound obtained from phthalic chloride and ammonia is really orthocyanobenzoïc acid. Phthalic diamide is formed by the action of ammonia on diethyl phthalate. A. R. L.

Acids occurring in Petroleum. By R. ZALOZIECKI (*Chem. Zeit.*, 16, 905—907).—The author, having experimented with these compounds, comes to the conclusion that Aschan's theory, which places them amongst the hexahydro-aromatic-carboxylic acids, must not be accepted without further proof. L. DE K.

Specific Rotatory Power of the Phenyldibromopropionic acids. By C. LIEBERMANN (*Ber.*, 26, 245—252).—The author has reexamined the optically active phenyldibromopropionic acids obtained

by Meyer (this vol., i, 93), who gave the specific rotatory power $[\alpha]_D = -13.1^\circ$ and $+14^\circ$. By employing only 1 mol. of strychnine to 2 mols. of the acid, and by a systematic fractional precipitation of the two optical antipodes so obtained, he has obtained a more complete separation. The highest specific rotations were $[\alpha]_D = +68.3^\circ$ and $[\alpha]_D = -45.8^\circ$. The other fractions gave intermediate numbers. According to Van't Hoff's hypothesis, phenyldibromopropionic acid is capable of existing in four optically active modifications and in two modifications of the racemic type. The author is engaged in a further study of these acids.

The author is also engaged in a similar investigation on the dibromo-derivatives of fumaric and maleic acids. He has prepared many alkaloid salts of these acids, which will shortly be described, but has not yet succeeded in separating either into its optically active modifications.

E. C. R.

Derivatives of the Cresolglycollic acids. By O. FORTE (*Gazzetta*, 22, ii, 525—546).—The author describes a large number of metallic salts of the three cresolglycollic acids. The *ammonium* salts, when heated above 110° , yield the corresponding amides. The *amide* of the ortho-acid, $C_9H_{11}O_2N$, melts at 128° , that of the meta-acid at 111 — 112° , whilst *paracresolglycollamide* melts at 126 — 127° . The *anilides* prepared from the ortho-, meta-, and para-acids melt at 110° , 95° , and 109° respectively; the *methyl* salts are colourless liquids of nauseating odours, and boil at 248° , 258° , and 257° respectively.

W. J. P.

Dibromogallic acid and its Salts. By A. BIÉTRIX (*Bull. Soc. Chim.* [3], 7, 411—417).—Dibromogallic acid (m. p. 139°) is conveniently prepared by adding gallic acid to a solution of bromine in chloroform. The *salts* are obtained by mixing solutions of metallic acetates with those of the acid; they are white substances, which are coloured strongly by heating. The *ammonium* salt melts at 175° with decomposition, the *sodium* salt melts at 185° with decomposition, the basic *zinc* salt, $(C_7H_2Br_2O_5)_2Zn_2$, commences to decompose at 110° , and melts at 189° . The basic *lead* salt, $(C_7H_2Br_2O_5)_2Pb_2$, decomposes at 160° , giving off white fumes, and leaving a black residue; and the normal *barium* salt melts between 195° and 200° . The *quinine* salt, $C_{20}H_{24}N_2O_2 \cdot C_6Br_2(OH)_3 \cdot COOH$, is formed as a white precipitate on mixing alcoholic solutions of the acid and of quinine; it is soluble in water, forming a rose-coloured solution, and melts with decomposition at 182 — 183° . The *strychnine* salt, $C_{21}H_{20}N_2O_2 \cdot C_6Br_2(OH)_3 \cdot COOH$, commences to decompose at 140° , and melts at 190° .

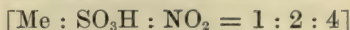
A. R. L.

Constitution of the Iodides of Aromatic Sulphonic acids. By R. OTTO and J. TRÖGER (*Ber.*, 26, 154—155).—When considered in the light of the arguments recently advanced by Selivanoff (this vol., i, 192), the compounds previously described by the authors (*Abstr.*, 1891, 718) as sulphonic iodides would appear to be more correctly denoted "iodyl" derivatives; as a matter of fact, they behave, in most cases, as if they were mixed anhydrides of sulphinic

and hypiodous acids, the compound $C_6H_5SO_2I$, for example, yielding iodoform, iodophenol, and phenyl bisulphide, on treatment with sodium ethoxide, phenoxide, and mercaptide respectively, as well as the salt of benzenesulphinic acid.

F. S. K.

Cryoscopic Studies in the Benzene Series. By J. HAUSSE (Bull. Soc. Chim. [3], 7, 516—523).—The author finds that certain sulphonic acids of benzene exhibit, in aqueous solutions, molecular depressions far in excess of the constant 19, which holds for the majority of organic substances; the molecular depressions, in fact, approximate to those obtained with the strong monobasic acids. Benzenesulphonic acid gave a mean value of the depression of the freezing point $C/P = 0.227$, the product of which, by the molecular weight, gives the constant 35.8. Nitrotoluenesulphonic acid



gave the constant 35.4, and its sodium salt gave 34.7; whilst nitrosulphobenzonic acid $[COOH : SO_3H : NO_2 = 1 : 2 : 4]$ gave the constant 38.5, its monopotassium salt (modification A) gave 39.9, and modification B gave 41.9.

The *silver* salt of the 1 : 2 : 4-nitrotoluenesulphonic acid crystallises with 1 mol. H_2O , and the *ethyl* salt melts at 68—69°. The *potassium* salt, $COOH \cdot C_6H_3(NO_2)_3 \cdot SO_3K$ (modification A), crystallises in prisms with 1 mol. H_2O . This salt passes into modification B, which crystallises in rhombic tables with 2 mols. H_2O , (1) when it is heated at 280—290° for some hours and then crystallised from water; (2) when, after being dried at 140°, it is heated with phosphoric chloride at 175° for 20 minutes; (3) when it is crystallised in the presence of potassium or ammonium chloride.

A. R. L.

Preparation of Pure Ethyl Benzenesulphinate and Ethyl Paratoluenesulphinate. By R. OTTO (Ber., 26, 308—310).—The ethyl benzenesulphinate and paratoluenesulphinate, formerly described by the author and Rössing (Abstr., 1885, 1231), were contaminated with phenylsulphone and tolylsulphone formates. The author has obtained the pure compounds from the product of the action of an alkali salt of the sulphinic acid and ethyl chlorocarbonate as follows:—The ethyl sulphinate is precipitated with water, the mixture rendered faintly alkaline with soda and extracted with petroleum (b. p. 30—40°). The petroleum extract is washed with dilute soda and then with water, and distilled, when the ethyl sulphinate is obtained in a pure condition. The properties of the two compounds have already been described. Ethyl benzenesulphinate has a sp. gr. at 20° = 1.1410; the toluenesulphinate has a sp. gr. = 1.1212.

E. C. R.

Behaviour of Indigo when heated with Alkalis. By K. HEUMANN and C. BACHOFEN (Ber., 26, 225—229; compare Abstr., 1891, 456).—The product formed when indigotin is fused with potash does not contain indigo-white, as it yields no precipitate when it is mixed with dilute acid. It was, on the other hand, shown to give the reactions described by Baeyer as typical of indoxyl. This sub-

stance is also formed when indigo is boiled with aqueous potash of sp. gr. 1.45.

Indoxylazobenzenesulphonic acid, a new substance, was obtained as the potassium salt, $C_{14}H_{10}N_3O_4SK$, by adding a solution of the fused mass in dilute sulphuric acid to an aqueous solution of paradiazo-benzenesulphonic acid. When dried, it forms green crusts with a metallic lustre; these yield a brownish-red powder, which, when rubbed, acquires a green, metallic lustre. It dyes silk and wool reddish-yellow in feebly acid solution, is decolorised by zinc-dust in alkaline solution, and decomposes suddenly when heated above 230° .

C. F. B.

Derivatives of Diphenyltrichlorethane and their conversion into Stilbene. By K. ELBS (*J. pr. Chem.* [2], 47, 44—79; compare Abstr., 1889, 713).—Sufficient evidence has now been obtained to enable the author to state generally that compounds of the formula $X_2CH \cdot CCl_3$, in which X is the radicle of an aromatic hydrocarbon, a phenol, or a phenetol, are converted into compounds of the formula $X \cdot CH : CH \cdot X$, by heating their alcoholic solutions with zinc-dust. In this way, stilbene, paradimethylstilbene (b. p. $304\text{--}305^\circ$), and metatetramethylstilbene have been obtained (Abstr., 1889, 713).

Diparaxyldichlorethylene melts at 93° , not 95° (*loc. cit.*); with zinc-dust, it yields paratetramethylstilbene [$Me_2 = 2 : 5$] (m. p. 157°).

Dipseudocumyltrichlorethane, $CCl_3 \cdot CH(C_6H_2Me_3)_2$, obtained by the action of chloral hydrate on pseudocumene in presence of strong sulphuric acid, crystallises in colourless prisms, melts at 143° , and dissolves sparingly in alcohol, but freely in carbon bisulphide, chloroform, and acetone. Alcoholic potash converts it into *dipseudocumyl-dichlorethylene*, $CCl_2 \cdot C(C_6H_2Me_3)_2$, which crystallises in colourless prisms, melts at 118° , and dissolves in alcohol, benzene, carbon bisulphide, and chloroform; the *disulphonic acid*, $CCl_2 \cdot C(C_6HMe_3 \cdot SO_3H)_2$, and its *barium* (with $4\frac{1}{2}$ mols. H_2O) and other salts, were prepared; the acid crystallises in white, hygroscopic needles, and is easily oxidised by potassium permanganate to *dipseudocumylketodisulphonic acid*, $CO \cdot C(C_6HMe_3 \cdot SO_3H)_2$, whose *barium* salt was prepared.

Hexamethylstilbene, $C_2H_2(C_6H_2Me_3)_2$ [$Me_3 = 2 : 4 : 5$], obtained by the general method from dipseudocumyltrichlorethane, crystallises in slender, white needles or flat prisms, melts at 161° , and dissolves sparingly in alcohol, but more freely in benzene, carbon bisulphide, and chloroform; it has a violet fluorescence, both in the solid condition and in solution. A *picrate* (crystallising with benzene) was prepared; it melts at 123° . The *bromide*, $C_2H_2Br_2(C_6H_2Me_3)_2$, crystallises in nacreous, colourless laminae, melts at $238\text{--}243^\circ$ with decomposition, and dissolves sparingly in alcohol, but easily in ether, chloroform, carbon bisulphide, and benzene; during the bromination, *bromo-symmetrical-dipseudocumylethane*, $C_2H_3Br(C_6H_2Me_3)_2$, melting at 177° , and *bromo-hexamethylstilbene bromide*, $C_6H_2Me_3 \cdot CHBr \cdot CHBr \cdot C_6HMe_3Br$, melting about 240° , were also obtained. During the reduction of dipseudocumyltrichlorethane, a small quantity of *asymmetrical dipseudo-cumylethane* (m. p. $117\text{--}120^\circ$) is formed.

α -*Dinaphthostilbene*, $C_2H_2(C_{10}H_7)_2$, is prepared by the reduction of α -dinaphthyltrichlorethane (for the preparation of which a new method is detailed; compare Grabowski, Abstr., 1878, 508); it is separated from the asymmetrical α -dinaphthylethane which accompanies it by crystallisation from glacial acetic acid, in which it is less soluble, and purified by conversion into the *picrate*, $C_2H_2(C_{10}H_7)_2 + 3C_6H_3N_3O_7$, which melts at 210° . α -Dinaphthostilbene crystallises in yellowish, silky laminæ, melts at 161° , and dissolves sparingly in alcohol, more freely in ether and glacial acetic acid, and easily in chloroform, carbon bisulphide, and benzene; its solutions fluoresce violet; oxidation converts it into 1-naphthoic acid. The *bromide* crystallises in colourless needles and laminæ, melts at 211° , and dissolves best in benzene.

Asymmetrical α -dinaphthylethane crystallises in colourless laminæ, melts at 136° , and is more soluble than dinaphthostilbene; its solutions fluoresce violet. It yields no *picrate*. *Dibromodinaphthylethane* melts at 215° and is sparingly soluble.

Concerning *paradihydroxystilbene* and the *nitrohydroxydiphenyltrichlorethanes*, see Abstr., 1889, 997.

β -*Dinaphthyloxidetrichlorethane*, $CCl_3 \cdot CH < \begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix} > O$, is the product of the condensation of chloral hydrate and β -naphthol by sulphuric acid; it crystallises in large, colourless, strongly-refractive prisms, melts, with decomposition, at 241° , and dissolves best in boiling chloroform and xylene. Reduction converts it into ethylidene- β -dinaphthylene oxide (m. p. 273° ; Abstr., 1887, 271). α -*Dinaphthyloxidetrichlorethane*, from α -naphthol and chloral hydrate, crystallises in prisms and melts at 238 – 239° with decomposition; it is being investigated.

Dianisyltrichlorethane [$CH \cdot CCl_3 : OMe = 1 : 4$], the product of the condensation of chloral hydrate and anisoil, crystallises in prisms, melts at 92° , and is freely soluble. By reduction, it yields *diparamethoxystilbene*, which fluoresces violet (compare Kopp, Abstr., 1892, 718).

α -*Diethoxynaphthyltrichlorethane*, $CCl_3 \cdot CH(C_{10}H_6 \cdot OEt)_2$, from chloral hydrate and 1-naphthyl ethyl ether, generally separates from its solutions as a crystalline powder; it melts at 198 – 200° , and dissolves best in xylene and benzene; it does not fluoresce.

α -*Diethoxydinaphthostilbene*, $C_2H_2(C_{10}H_6 \cdot OEt)_2$, obtained by reducing the last compound, exists in two modifications; the stable form crystallises in sulphur-yellow tables, the unstable form in colourless needles; both fluoresce blue when solid and in solution. The unstable form is obtained by recrystallising the stable form from boiling glacial acetic acid or alcohol; it gradually changes into the stable form at 100° , and rapidly at 160 – 170° . The stable modification melts at 185 – 186° , and boils at a higher temperature undecomposed; it dissolves best in boiling xylene and benzene. The *picrate* (2 mols. *picric acid*) melts at 236 – 238° . The *bromide* has not been purified.

β -*Diethoxydinaphthyltrichlorethane*, from 2-naphthyl ethyl ether and chloral hydrate, is a crystalline powder; it melts with decomposition at 206° , dissolves best in boiling xylene and benzene; by reduction,

it yields a substance which melts at 186° , but has not been satisfactorily identified as β -diethoxydinaphthostilbene.

The paper concludes with a table, showing the solubility of the above compounds in alcohol. A. G. B.

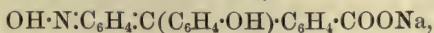
Condensation Products of Amidophenols. By E. HAEGLE (*Ber.*, **26**, 394).—Benzylideneparamidophenol melts at 183° , hydroxybenzylideneorthoamidophenol at 185° , and cinnamylideneparamidophenol at 203° , instead of at 163° , 175° , and 223° respectively, as previously stated (compare Abstr., 1892, 1451). J. B. T.

Solubility of Triphenylmethane in Benzene. By C. E. LINEBARGER (*Amer. Chem. J.*, **15**, 45–49).—The solubility of triphenylmethane in benzene is shown in the following table.

Temperature.	Parts CHPh_3 per 100 parts C_6H_6 .	Temperature.	Parts CHPh_3 per 100 parts C_6H_6 .
3.9°	3.90	37.5°	10.48
4.0	4.06	42.0	19.61
12.5	5.18	44.6	22.64
13.0	5.51	50.1	30.64
16.1	6.83	55.5	40.51
19.4	7.24	71.0	140.0
23.1	8.95	76.2	319.67

Changes of curvature occur at 3.9° , 27.5° , 76.2° , and 94.3° . At 3.9° , there exist together benzene (solid), a molecular compound of triphenylmethane and benzene, $\text{CHPh}_3 \cdot \text{C}_6\text{H}_6$ (solid), a solution of triphenylmethane in benzene, (liquid), and a mixture of the vapour of triphenylmethane and benzene (gas). At 37.5° , the benzene is no longer solid, and the molecular compound has begun to decompose, so that triphenylmethane (solid) is present. The molecular compound melts at 76.2° in a closed tube. The melting point of triphenylmethane is 94.3° . JN. W.

Phenolphthaleïn. By P. FRIEDLÄNDER (*Ber.*, **26**, 172–179).—The constitutional formula ascribed by Baeyer to phenolphthaleïn, namely, $\text{CO} < \text{C}_6\text{H}_4 > \text{C}(\text{C}_6\text{H}_4 \cdot \text{OH})_2$, explains all the reactions in a satisfactory manner, but it is difficult to understand how the salts of such a colourless substance should be colouring matters if they are formed by the simple substitution of a metal for the hydrogen of one of the hydroxyl groups; the author has, therefore, endeavoured to ascertain whether, in the formation of the salts, an intramolecular change takes place with formation of a quinone derivative having the constitution $\text{O} : \text{C}_6\text{H}_4 : \text{C}(\text{C}_6\text{H}_4 \cdot \text{ONa}) \cdot \text{C}_6\text{H}_4 \cdot \text{COONa}$, which would correspond with the quinone formulæ proposed by Nietzki for rosaniline and rosolic acid. To test the truth of the supposition, an alkaline solution of phenolphthaleïn was treated with hydroxylamine, with the result that an oxime of the sodium salt,



was readily obtained on adding acetic acid. The oxime separates as a bright yellow, crystalline precipitate, which is purified by washing with water and alcohol. It is scarcely soluble in the common solvents and melts at 212° with decomposition. It is dissolved by alkalis with the formation of two series of salts, and yields a *hydrochloride*, and a crystalline *acetyl* derivative insoluble in alkali. When hydrolysed with dilute sulphuric acid, it is converted into amidophenol and *parahydroxyorthobenzoylbenzoic acid*, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, which crystallises in white plates, and melts with decomposition at 210° , the former being probably obtained by an intramolecular change from the phenylhydroxylamine which should be the first product of the hydrolysis. Fusion with alkali gives similar results, the benzoylbenzoic acid being further resolved into benzoic and parahydroxybenzoic acids.

H. G. C.

Trihydroxyaurin from Catechol. By N. CARO (*Ber.*, 26, 254—255; see also *Abstr.*, 1892, 855 and 1469).—*Methylenedicatichol*, $\text{CH}_2[\text{C}_6\text{H}_3(\text{OH})_2]_2$, is obtained by boiling a solution of catechol, formaldehyde, and a few drops of hydrochloric or sulphuric acid for some time. It crystallises in needles, melts at 220° with decomposition, and is easily soluble in alkalis.

Trihydroxyaurin, $\text{O} < \text{C} \begin{array}{c} \text{C}_6\text{H}_3\cdot\text{OH} \\ | \\ \text{C}[\text{C}_6\text{H}_3(\text{OH})_2]_2 \end{array}$, cannot be obtained pure by the condensation of methylenedicatichol with catechol. It is obtained by Nencki and Schmidt's method for the preparation of aurines (*J. pr. Chem.* [2], 23, 547). It crystallises in leaflets, dissolves in alcohol with a beautiful red coloration, and yields dyes with mordants.

E. C. R.

Aniselines, a New Class of Colouring Matters, and their Constitution. By P. MONNET (*Bull. Soc. Chim.* [3], 7, 523—527).—As is known, rhodamines are obtained by the interaction of dialkylmetamidophenols and phthalic anhydride; the *aniselines* are formed by heating the potassium derivatives of the rhodamines with alkyl chlorides.

The simplest anisoline, $\text{CO}\cdot\text{O} > \text{C} \begin{array}{c} | \\ \text{C}_6\text{H}_4 \end{array} > \text{C}[\text{C}_6\text{H}_3(\text{OEt})\cdot\text{NEt}_2]_2$, derived from diethylmetamidophenol, is obtained by dissolving the corresponding rhodamine hydrochloride in boiling water, and pouring the solution into one of potassium hydroxide. The potassium salt which separates is dried at 100° , and heated in a sealed tube with ethyl chloride and alcohol at 120° for four hours. The melt is poured into water, and the solution heated to expel the alcohol; an excess of hydrochloric acid is now added, and the *hydrochloride* finally precipitated with sodium chloride; it is a green powder with metallic lustre. In preparing benzylated aniselines, the mixtures must be heated to 140° ; they readily yield sulphonic acids.

The aniselines colour unmordanted fibres (especially cotton) a magnificent reddish-violet of great fastness.

A. R. L.

Substitution Products of the Naphthyl Ethers. By J. SACHS (*Ber.*, 26, 252—254).—*Dichloro- β -dinaphthyl oxide*, $\text{C}_{20}\text{H}_{12}\text{Cl}_2\text{O}$, is

prepared by the action of phosphorus pentachloride on β -dinaphthyl oxide. It crystallises in beautiful, colourless prisms, and melts at 128° .

Dibromo- β -dinaphthyl oxide is obtained by adding bromine to a solution of the β -dinaphthyl oxide in carbon bisulphide. It crystallises with 3 mols. of benzene in stout, transparent prisms which melt at 89° . When freed from benzene by heating at 80° , it melts at 132° .

Dinitro- β -dinaphthyl oxide is obtained by adding nitric acid to a solution of the oxide in acetic acid. It crystallises in indistinct, yellow needles, and melts at 145° .

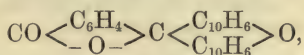
Hexanitro- β -dinaphthyl oxide is obtained by adding the oxide to well cooled fuming nitric acid. It forms yellow crystals, and decomposes at 270° without melting.

Dibromedinitro- β -dinaphthyl oxide, obtained by brominating the dinitro-compound, crystallises in indistinct, yellow prisms, and melts at 87° .

Dichlorodinitro- β -dinaphthyl oxide is an orange-yellow, crystalline compound, and melts at 76° .

Dibromo- α -dinaphthyl oxide separates in beautiful colourless crystals which do not contain benzene, and melts at 158° . E. C. R.

Compounds of Phthalic acid with Phenols. By R. MEYER (*Ber.*, 26, 204—210; compare Abstr., 1891, 1029, and especially 1485, of which paper the present one is but an amplification).—The product of the action of β -naphthol on phthalic chloride is not, as hitherto supposed, β -naphthofluoran,



but consists mainly of β -naphthyl phthalate, $\text{C}_6\text{H}_4(\text{COOC}_{10}\text{H}_7)_2$ or $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O} \end{smallmatrix} > \text{C}(\text{OC}_{10}\text{H}_7)_2$, mixed with a small quantity of the fluoran.

The phthalate was identified by hydrolysing it by treatment with potash, when it yielded phthalic acid and β -naphthol. β -Naphthofluoran forms colourless needles, and melts at 293° ; its solution in sulphuric acid exhibits a reddish-yellow fluorescence. It may also be prepared, although only in small quantity, by heating phthalic anhydride with β -naphthol for some time at 220° . α -Naphthofluoran has already been obtained by Grabowski (*Ber.*, 4, 661); the author confirms his results. With pseudocumenol, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{OH}$ [$\text{Me}_3 : \text{OH} = 1 : 2 : 4 : 5$], melting at 67° , phthalic chloride yields the corresponding phthalate, in brilliant needles melting at 118 — 119° ; no fluoran is formed. Paracresol also yields the phthalate in brilliant, colourless prisms melting at 83 — 84° ; a trace of a fluoran was possibly formed, but only a very feeble fluorescence was exhibited on dissolving the crude product of the reaction in sulphuric acid. C. F. B.

Benzeneazonaphthalene and Tolueneazonaphthalene. By R. NIETZKI and R. ZEHNTER (*Ber.*, 26, 143—145).—*Benzene- α -azo-*

naphthalene, $C_{16}H_{12}N_2$, prepared by diazotising benzene- α -azonaphthylamine and decomposing the product with boiling alcohol, crystallises in dark red plates, melts at 63.5° , and dissolves in concentrated sulphuric acid with a reddish-violet coloration. The corresponding *hydrazo*-compound, $NHPh \cdot NH \cdot C_{10}H_7$, prepared by reducing the azo-derivative with alcoholic ammonium sulphide, crystallises in yellowish plates, melts at 125° , and oxidises very readily on exposure to the air; its *diacetyl* derivative melts at 264° .

Diamidophenylnaphthalene is formed when benzenehydrazonaphthalene is treated with mineral acids: it crystallises in greyish plates, and melts at 64° . The *hydrochloride*, $C_{16}H_{14}N_2 \cdot 2HCl$, is a colourless, crystalline compound; the *sulphate* is sparingly soluble in water. The *diacetyl* derivative, $C_{20}H_{18}N_2O_2$, crystallises in needles, and melts at 285° . The *tetrazo*-derivative combines readily with naphthionic, salicylic, and naphtholsulphonic acids yielding azo-dyes, which can be fixed on unmordanted cotton, but which are of little value as dyes compared with the corresponding derivatives of benzidine and tolidine.

Orthotoluene- α -azonaphthalene, $C_{17}H_{14}N_2$, obtained from orthotoluene- α -azonaphthylamine, crystallises in small, red plates, and melts at 52° ; the corresponding *hydrazo*-compound, $C_{17}H_{16}N_2$, melts at 107° , and forms a *diacetyl* derivative melting at 252° .

Diamidotolyl-naphthalene, prepared by treating the *hydrazo*-compound with mineral acids, melts at 76° , forms a sparingly soluble *sulphate*, and a *hydrochloride* of the composition $C_{17}H_{16}N_2 \cdot 2HCl$; its *diacetyl* derivative, $C_{21}H_{20}N_2O_2$, melts at 261° with decomposition. The *tetrazo*-derivative yields azo-dyes, which are similar to those obtained from diamidophenylnaphthalene.

F. S. K.

Sulphonic Derivatives of Naphthalene. By R. OTTO, A. RÖSSING, and J. TRÖGER (*J. pr. Chem.* [2], **47**, 94—104).—The first part of this paper consists of a review of our knowledge of 1- and 2-naphthalenesulphinic acids and their reactions (compare this Journal, 1877, i, 315; *Zeits. Chem.*, 1869, 710; *Abstr.*, 1892, 623).

α -Naphthylmethylsulphone forms rhombic crystals, of which full measurements are here given; it melts at 102 — 103° . β -Naphthylmethylsulphone melts at 142 — 143° , not 139 — 140° (*Abstr.*, 1892, 623).

α -Naphthylethylsulphone, from sodium α -naphthylsulphinate and ethyl iodide, crystallises in small needles, melts at 88 — 89° , and dissolves easily in alcohol, glacial acetic acid, and benzene, but not in water. β -Naphthylethylsulphone, from sodium β -naphthylsulphinate and ethyl bromide, forms ill-defined crystals, melts at 43 — 45° , and dissolves in ether, alcohol, and benzene, but not in water.

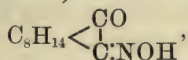
A. G. B.

Constitution of Camphor, Oil of Turpentine, and of their Principal Derivatives. By L. BOUVEAULT (*Bull. Soc. Chim.* [3], **7**, 527—538).—A polemical paper. The various constitutional formulæ which have been assigned to the members of the terpene series are discussed, and the author's line of argument finally leads him to the adoption of the formulæ proposed by Wallach.

A. R. L.

Novel Transformation of Camphor into Camphoric Acid.

By A. ANGELI (*Ber.*, **26**, 58—50).—Nitrosocamphor,



is readily converted into the imide of camphoric acid (Winzer, *Abstr.*, 1890, 1152) when it is heated on the water-bath for five minutes with concentrated sulphuric acid (10 parts). Seeing, therefore, that the carboxyl groups in camphoric acid originate from the group $\text{—CO}\cdot\text{CH}_2\text{—}$ in camphor, the author is of opinion that the relation of camphor to camphoric acid is a simple one, involving no intramolecular changes.

A. R. L.

Conversion of Nitrosocamphor into Camphoric Imide. Camphordioximes.

By O. MANASSE (*Ber.*, **26**, 241—245).—The author confirms Angeli's results (preceding abstract). Nitrosocamphor is converted into camphoric imide by treating it with concentrated sulphuric acid; by heating it at 100° in a solution of acetic acid and acetic anhydride saturated with hydrogen chloride, or by warming it with concentrated hydrochloric acid. By the last method only a small yield is obtained, as the greater part is converted into camphoramic acid, $\text{COOH}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{NH}_2$.

Camphordioximes, $\text{C}_8\text{H}_{14}(\text{C}\cdot\text{NOH})_2$.—The author has obtained three isomeric dioximes. The α - and β -dioximes are obtained by the action of hydroxylamine acetate on nitrosocamphor; the γ -dioxime is obtained by the action of free hydroxylamine. The α - and β -dioximes are separated by shaking the mixture with cold alcohol, which only dissolves the α -dioxime. The α -dioxime melts at $181\text{—}182^\circ$ with decomposition; the β -dioxime at $220\text{—}221^\circ$ with decomposition. The γ -dioxime crystallises in white leaflets, melts at $131\text{—}132^\circ$ without decomposition, and when further heated is converted into the α -dioxime.

The α - and β -dioximes, when heated for six hours with concentrated sulphuric acid at 65° , are unaltered, whereas the γ -dioxime under the same conditions is converted into the α -dioxime.

E. C. R.

Terpenes and their Derivatives. By J. W. BRÜHL and R. BRAUNSCHWEIG (*Ber.*, **26**, 284—292; see also *Abstr.*, 1892, 1100; *Trans.*, 1892, 1089).—Camphoric acid may be distilled unchanged in a rapid stream of carbonic anhydride or other indifferent gas. The best method of preparing camphoric anhydride is to heat camphoric acid in a slow stream of carbonic anhydride until water ceases to pass over, and then to distil the anhydride in a rapid stream of the gas.

Orthoalkyl hydrogen camphorates are very easily obtained by heating camphoric anhydride with an alcohol, or the sodium derivative of an alcohol.

Orthomethyl and orthoethyl hydrogen camphorates are obtained by heating camphoric anhydride with methyl or ethyl alcohol in a closed vessel at 160° for 12 hours. Orthomethyl and orthoethyl sodium camphorates are obtained by distilling a mixture of camphoric anhydride, methyl or ethyl alcohol, and sodium.

Orthomethyl hydrogen camphorate crystallises from water in crystals which have already been described. It has now been obtained from light petroleum in two other forms, which are hemihedral, and belong to the rhombic system,

$$a : b : c = 0.7855 : 1 : 0.4949.$$

The one form is prismatic, of rhombic habit; the other tabular, of hexagonal habit.

Allomethyl hydrogen camphorate crystallises from light petroleum in beautiful prismatic crystals belonging to the rhombic system, $a : b : c = 0.7815 : 1 : 0.7609$.

The ethereal salts of camphoric acid, with the exception of the orthoethyl salt, distil unchanged under diminished pressure, and the following constants were determined.

The orthomethyl salt boils at 198.5° under 15 mm., and melts after distillation at 77° . The allomethyl salt boils at 193° under 15 mm., and melts at 86° . The orthoethyl salt boils at 204° under 14 mm. pressure, with partial decomposition. The alloethyl salt boils at 196.5° under 13 mm., and melts at 57° .

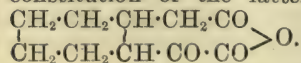
The author points out that the above synthesis of the ortho-ethereal salts from camphoric anhydride is a weighty argument in favour of the view that camphoric acid is a dicarboxylic acid.

Ethyl hydrogen camphorate, when warmed with phenylhydrazine, yields two isomeric compounds of the formula $C_{17}H_{22}N_2O_2$, which may be separated by fractional crystallisation from light petroleum. The one compound crystallises in nodules, and melts at 137° ; the other in slender needles, and melts at $126-127^\circ$. E. C. R.

Action of Phenylhydrazine on Cantharidin. By L. SPIEGEL (*Ber.*, 26, 140—143; compare *Abstr.*, 1892, 999; and this vol., i, 40).—When cantharidinphenylhydrazone is treated with bromine in boiling glacial acetic acid solution, it is converted into a compound of the composition $C_{16}H_{16}N_2Br_2O_3$, which crystallises in slender, colourless needles, and melts at 245° (corr.); under the same conditions, the hydrate of the hydrazone yields not only the dibromo-derivative melting at 245° , but also a substance which crystallises from alcohol in yellowish prisms, melts at 194° (corr.), and is probably a *diacetyl* derivative of the composition $C_{16}H_{16}N_2Br_2O_4Ac_2$.

A bright yellow substance, which seems to be a mixture of the nitro-, $C_{16}H_{17}N_2O_3 \cdot NO_2$, and dinitro-, $C_{16}H_{16}N_2O_3(NO_2)_2$, derivatives, is formed when cantharidinphenylhydrazone is treated with ice-cold nitric acid; it crystallises in slender, canary-yellow needles, does not melt at $320-330^\circ$, and gives an intense red coloration with alkalis; on reduction with stannous chloride and hydrochloric acid, it yields cantharidinimide.

When cantharidinphenylhydrazone is reduced with sodium amalgam and acetic acid in alcoholic solution, it gives cantharidin; the constitution of the latter is possibly represented by the formula



F. S. K.

Action of Alkalis on the Alkyl Iodides of Pyridine and similar Bases. By H. DECKER (*J. pr. Chem.* [2], 47, 28—44; compare Abstr., 1892, 729, 879).—1-Methyl-2-pyridone (Abstr., 1892, 729) boils at 250°, not 240° (Pechmann and Baltzer, Abstr., 1892, 209). 1-Ethyl-2-pyridone boils at 249—250°, not 246—248° (*loc. cit.*). 1'-Methyl-2'-quinolone boils at 324° (728 mm.); this compound has been described by Friedländer and Müller as methylpseudocarbostyryl (Abstr., 1887, 977), and is probably also identical with a compound (m. p. 73°) obtained by Bernthsen and Hess (Abstr., 1885, 558) and with one (m. p. 72—75°) obtained by Ostermayer (Abstr., 1885, 813). 1'-Ethyl-2'-quinolone (Friedländer and Müller's ethylpseudocarbostyryl; Abstr., 1885, 988) boils at 316—318°, and remains superfused for a long time. 1'-Methylisquinolone melts at 38—40°; its *platinochloride* (with 2 mols. H₂O) is described.

1'-Methylnitroisquinolone is obtained by oxidising nitrosoquinoline methiodide in alkaline solution, best by potassium ferricyanide; it crystallises in yellow needles, melts, but not sharply, at 120°, and dissolves easily in benzene, ether, and alcohol; its *platinochloride* melts with decomposition between 165° and 170°.

The preparation of the compounds mentioned in this abstract can be quantitatively effected by titrating an alkaline solution of potassium ferricyanide with a solution of the quinoline alkyl iodide until the yellow colour of the ferricyanide disappears. A. G. B.

Combination of Quinoline with Silver Haloids. By R. VARET (*Compt. rend.*, 116, 60—62; compare Abstr., 1891, 732 and 838, and 1892, 1483).—When quinoline is heated at 60°, it dissolves considerable quantities of silver cyanide without appreciable reduction, and when the solution cools it deposits large, transparent crystals of quinoline argentocyanide, AgCN, 2C₉H₇N. This compound is decomposed by water and by heat; it dissolves readily in warm quinoline, but if the temperature is raised much above 60° the silver cyanide separates as a flocculent precipitate.

Silver bromide, chloride, and iodide are almost insoluble in quinoline, but if triturated with the latter and allowed to remain in contact with it for some time in the dark and out of contact with air, compounds of the general composition AgX, C₉H₇N are formed. Quinoline argentobromide and quinoline argentochloride crystallise in slender needles; the argentoiodide forms a white, amorphous compound. They are all decomposed by water and by heat, and alter when exposed to air and light. C. H. B.

Synthesis of Ring Compounds from Benzene Derivatives with Open Side-chains. By P. SCHAD (*Ber.*, 26, 216—224).—The following new synthesis of indazole is probably more convenient than those previously described. A solution of isatin and sodium nitrite in dilute aqueous soda is poured into cooled dilute sulphuric acid, the liquid is saturated with sulphurous anhydride, and excess of stannous chloride is finally added; indazolecarboxylic acid then separates, orthodiazo- and orthohydrazine-phenylglyoxylic acids having been doubtless formed as intermediate product. The acid,

when heated above its melting point, loses carbonic anhydride, and forms indazole. *Indazolecarboxylic acid*, $C_6H_4<\overset{C(COOH)}{\underset{N}{|}}>N$, forms

transparent, rhombic plates, melts with decomposition at 258—259°, yields an *ammonium salt*, $C_7H_5N_2 \cdot COONH_4 + \frac{1}{2}H_2O$, as sparingly soluble, colourless needles, and insoluble salts with solutions of salts of the heavy metals; with acetic anhydride, it yields an acetyl derivative, but it does not form a nitroso-derivative. *n-Methylindazole*,

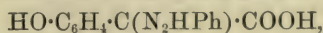
$C_6H_4<\overset{CH}{\underset{N}{|}}>NMe$, is obtained by heating indazole with methyl iodide at 100° in a tube; it forms lustrous plates melting at 35°.

The *nitrosamine* of *orthomethylamidophenylglyoxylic acid*, $C_9H_8N_2O_4$, was obtained by treating methylpseudoisatin with nitrous acid in the cold; it crystallises in groups of yellowish-white needles, melts with decomposition at 107°, gives Liebermann's reaction, and is very unstable, the nitroso-group being readily eliminated under the influence of reducing agents, with re-formation of the original acid. *Para-*

methylindazole, $C_6H_3Me<\overset{CH}{\underset{N}{|}}>NH$, and its *carboxylic acid* may be obtained from paramethylisatin in the same way as the above-mentioned compounds from isatin itself. The acid forms colourless needles, melting with decomposition at 285—286°; the indazole colourless needles melting at 115°.

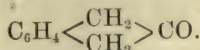
β -*Diamidodiphenic acid*, $C_{14}H_{12}N_2O_4$, obtained by reducing β -dinitrodiphenic acid (from phenanthraquinone and nitric acid), is a very insoluble substance, and chemically very inert; by acidifying a hot solution of its ammonium salt with acetic acid, it is obtained in small, colourless needles which char above 300°. It is probably the *ortho*-diamido-compound, for when heated with lime it yields ammonia; now orthodiamidodiphenyl is known to be converted into carbazole by the action of heat, and carbazole yields ammonia when heated with lime.

The *phenylhydrazone* of *hydroxyphenylglyoxylic acid*,

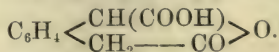


was prepared. The action of sodium phenolate on ethyl chloroxalate results in the formation of diphenyl oxalate.

Calcium phenylenediacetate, when distilled, chars, but decomposes to some extent into calcium carbonate and β -ketohydrindene,;



This crystallises in colourless needles, and melts at 58°; its *phenylhydrazone* forms yellowish tables melting at 120°, and its *oxime*, C_9H_9NO , colourless needles, melting at 152°. When phenylenediacetic acid is mixed with red phosphorus, the mixture treated with bromine, and the bromo-acid thus formed is decomposed with water, it yields the *lactonic acid* of *phenylacetoglycollic acid*,

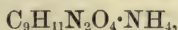


This melts at 140° , and crystallises from water with $1\frac{1}{2}\text{H}_2\text{O}$ in groups of needles which melt at 85° . By digesting its aqueous solution with barium carbonate, the *barium salt*, $(\text{C}_{10}\text{H}_7\text{O}_4)_2\text{Ba} + 4\text{H}_2\text{O}$, may be obtained in colourless plates. When boiled with an alkali, the lactone ring is broken, but, on neutralising the solution, a salt of phenylacetoglyoxylic acid is at once re-formed. C. F. B.

Glyoxalinedicarboxylic acids. By MAQUENNE (*Ann. Chim. Phys.* [6], **24**, 522—548; compare Abstr., 1890, 1439; 1891, 330).—*2-Ethyl- β -pyrazole-4 : 5-dicarboxylic acid* (*ethylglyoxalinedicarboxylic acid*), $\text{C}_7\text{H}_8\text{N}_2\text{O}_4 + \text{H}_2\text{O}$, is obtained when dinitrotartaric acid is treated with propaldehyde in presence of ammonia; it crystallises in colourless needles, loses its water at 2° , and decomposes into carbonic anhydride and 2-ethyl- β -pyrazole when heated more strongly.

2-Isopropyl- β -pyrazoledicarboxylic acid, $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_4 + \text{H}_2\text{O}$, prepared from isobutaldehyde in like manner, crystallises in prismatic needles, loses its water at 182° , and yields 2-isopropyl- β -pyrazole on distillation.

2-Isobutyl- β -pyrazoledicarboxylic acid, $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_4$, prepared from isovaleraldehyde, is a crystalline, sparingly soluble powder, and gives 2-isobutyl- β -pyrazole on distillation; the *ammonium salt*,



crystallises in slender needles.

2-Hexyl- β -pyrazoledicarboxylic acid, $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_4$, is formed from cœnanthaldehyde under the conditions already stated; it crystallises in small, yellow plates, and yields 2-hexyl- β -pyrazole melting at $45\text{--}46^{\circ}$ on distillation.

2-Phenyl- β -pyrazoledicarboxylic acid, $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4$, prepared from benzaldehyde, crystallises in lustrous plates, and is almost insoluble in water; the phenyl- β -pyrazole obtained from it has been described (*loc. cit.*). F. S. K.

4-Phenylpyrazole. By E. BUCHNER and M. FRITSCH (*Ber.*, **26**, 256—258; compare next abstract).—*4-Phenylpyrazole-3 : 5-dicarboxylic acid*, $\text{C}_3\text{N}_2\text{HPh}(\text{COOH})_2$, is prepared by heating methyl diazoacetate with methyl phenylpropionate or with methyl α -bromocinnamate at $80\text{--}90^{\circ}$ and hydrolysing the product; it crystallises from water in colourless needles, melts at 243° with decomposition, and is not affected by potassium permanganate in alkaline solution. Its constitution is shown by its failure to form a fluorescein derivative. The *calcium salt* crystallises with $4\text{H}_2\text{O}$. *4-Phenylpyrazole*, $\text{C}_3\text{N}_2\text{H}_3\text{Ph}$, is obtained by heating the carboxylic acid at $250\text{--}270^{\circ}$; it crystallises in needles, melts at 78° , boils at $280\text{--}290^{\circ}$, and reduces ammoniacal silver solution. The *hydrochloride* melts at $144\text{--}145^{\circ}$; the *platinochloride* crystallises with $2\text{H}_2\text{O}$; it softens at 193° with slight decomposition, solidifies on further heating, and melts at about 218° . The *benzoyl derivative* crystallises in needles melting at 59° .

J. B. T.

5-Phenylpyrazole. By E. BUCHNER and H. DESSAUER (*Ber.*, 26, 258—261; compare preceding abstract).—By the action of ethyl cinnamate on ethyl diazoacetate at 100°, *diethyl 5-phenylpyrazoline-3:4-dicarboxylate* is formed, and has been previously described as “ethyl cinnamodiazooacetate”; it melts at 79°, and yields ethyl phenylpyrazoledicarboxylate on treatment with bromine. The *silver salt* forms a lemon-coloured, flocculent precipitate. *Dimethyl phenylpyrazolinedicarboxylate* melts at 105°. The *3-ethyl-4-methyl salt*, prepared from methyl cinnamate and ethyl diazoacetate, melts at 76°. The *3-methyl-4-ethyl salt* from ethyl cinnamate and methyl diazoacetate, melts at 107°. The *amide*, $C_6H_5N_2(CONH_2)_2$, melts at 228° with decomposition. The *acid*, $\begin{array}{c} CHPh \cdot CH \cdot COOH \\ | \\ NH \cdot N : C \cdot COOH \end{array}$, melts at 178° with

decomposition, and, on reduction with sodium amalgam, yields *phenylpyrazolinedicarboxylic acid*, which is being further investigated.

5-Phenylpyrazole-3:4-dicarboxylic acid is formed by the oxidation of the pyrazolinedicarboxylic acid with potassium ferricyanide; it is deposited from ether in yellow crystals, melts at 243° with decomposition, is not acted on by potassium permanganate in alkaline solution, and gives the fluorescein reaction.

5-Phenylpyrazole, $C_3N_2H_3Ph$, is prepared by heating the preceding compound, or by distilling silver phenylpyrazolinedicarboxylate in a current of carbonic anhydride; it crystallises in colourless plates melting at 228°. The *silver salt* is sparingly soluble; the *hydrochloride* crystallises in needles melting at 215—218°; the *platinochloride* is orange-red and melts at 287°.

5-Phenylpyrazoline, $NH < \begin{array}{c} CHPh \\ N : CH \end{array} > CH_2$, is obtained from the hydrochloride as a yellow oil. The *hydrochloride* is prepared by boiling the dicarboxylic acid with hydrochloric acid; the simultaneous formation of hydrazine salts could not be detected; it is colourless and crystalline, melts at 162° with decomposition, reduces copper acetate solution, and, on treatment with bromine, yields 3-phenylpyrazole. The position of the phenyl group in the preceding compounds cannot be regarded as being definitely proved; the mutual attraction of the phenyl and imido-groups renders the formulæ given the more probable.
J. B. T.

Ammonium Derivatives of Azines. By O. FISCHER and E. FRANCK (*Ber.*, 26, 179—183).—It has previously been shown that ammonium derivatives of the azines may be obtained by the action of alkyl iodides on the azines (*Abstr.*, 1891, 1514), and the present paper gives a detailed account of the compounds obtained.

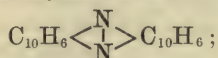
n-Methylnaphthophenazonium iodide, $C_{10}H_6 < \begin{array}{c} N \\ NMeI \end{array} > C_6H_4$, obtained by heating $\alpha\beta$ -naphthophenazine with methyl iodide, diluted with methyl alcohol or ether, under pressure for 10 hours at 130°, crystallises in brownish-red needles, which yield yellow solutions having a greenish-yellow fluorescence. When treated with silver oxide, it yields the corresponding *n-methylphenazonium hydroxide* in red plates, having a metallic lustre; it is somewhat unstable, melts with decom-

position at 175° , and yields reddish-yellow solutions having a brownish-yellow fluorescence. The corresponding *ethyl* derivatives are obtained in a similar manner, the *iodide* forming almost black needles, and melting at 150° with decomposition, and the *hydroxide*, cinnabar-red plates having a greenish shimmer, and melting at 185° when quickly heated.

Phenazine, when treated in a similar manner with methyl iodide and ethyl iodide, yields substances belonging to the group of per-iodides having the composition $C_{12}H_8N_2MeI_2$ and $C_{12}H_8N_2EtI_2$ respectively; they both form green crystals and yield iodoform with alcohol and sodium carbonate. The corresponding hydroxides could not be obtained pure.

H. G. C.

Naphthazines. By O. FISCHER and A. JUNK (*Ber.*, **26**, 183—187).—As already stated by Fischer and Hepp (*Abstr.*, 1890, 614), α -nitroso- β -naphthylamine, when heated with α -naphthylamine hydrochloride, is converted into asymmetrical $\alpha\beta$ -naphthazine,



this is purified by repeated crystallisations from benzene or ethyl benzoate, and then melts at 283° ; it forms orange-yellow, slender needles, which sublime with simultaneous carbonisation; the *hydrochloride* crystallises in dark red, felted needles. When heated with methyl iodide under pressure, it is converted into the *methiodide*, $C_{20}H_{12}N_2MeI$, which forms brown needles with a green, metallic shimmer, yields solutions in alcohol and acetic acid having a brown fluorescence, and dissolves in concentrated sulphuric acid with a corn-flower-blue colour. The corresponding hydroxide has not been obtained pure.

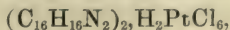
α -Nitroso- β -naphthylamine and β -naphthylamine yield the symmetrical $\alpha\beta$ -naphthazine already described by Mathes (*Abstr.*, 1890, 993), but the yield is very small. The chief product is a new $\alpha\beta$: $\beta\beta$ -naphthazine, which crystallises in woolly, orange-yellow needles, melts at 295 — 296° , and dissolves in concentrated sulphuric acid with a greenish-blue colour. Although its purple-violet solution in acetic acid shows no fluorescence, the benzene and ethyl benzoate solutions have a deep green fluorescence. The *hydrochloride* forms dark brown needles, and the *methiodide* brown needles with a violet shimmer, which yields a non-fluorescent red solution in alcohol and acetic acid.

Symmetrical $\alpha\beta$ -naphthazine may be prepared in an analogous manner to naphthophenazine (*Abstr.*, 1887, 1114), by dissolving $\beta\beta$ -dinaphthylnitrosamine in acetic acid and heating for an hour at 60 — 70° ; with methyl iodide, it yields a *methiodide* which crystallises in pale brown needles and dissolves in alcohol or acetic acid, forming a yellow solution with a grass-green fluorescence.

H. G. C.

Orthodiamine Derivatives. By O. FISCHER (*Ber.*, **26**, 187—204; compare *Abstr.*, 1892, 1472).—When orthamidoparaditolylamine is boiled for half an hour with acetic acid and acetic anhydride, the

acetyl derivative (Abstr., 1891, 434) is not formed, but the corresponding *anhydro-base*, $C_6H_4 < \begin{smallmatrix} N(C_7H_7) \\ N=CM_e \end{smallmatrix} >$; this crystallises in tufts of white needles, and melts at 94–95°; the *platinochloride*,



forms yellow prisms.

When β -phenylorthonaphthylenediamine is oxidised by dry distillation with lead oxide, yellow needles of $\alpha\beta$ -naphthophenazine, $C_{10}H_6 < \begin{smallmatrix} N \\ | \\ N \end{smallmatrix} > C_6H_4$, melting at 142°, are obtained. If the amine is boiled with alcoholic potash and carbon bisulphide, a thiocarbamide, $C_{17}H_{12}N_2S$, is formed; this crystallises in flat, colourless needles, melts at a temperature higher than the boiling point of sulphuric acid, dissolves in alkalis, and yields naphthophenazine when distilled with lead oxide.

n-Phenylmethylorthonaphthylenediamine, $NHMe \cdot C_{10}H_6 \cdot NHPh$, is obtained by heating phenylnaphthylenediamine with methyl iodide in methyl alcohol solution, under pressure at 100°, or by allowing the solution to remain for a long time at the ordinary temperature. It melts at 85°, crystallises in colourless plates, and yields a nitrosamine with nitrous acid. The corresponding *ethyl* compound, $C_{18}H_{18}N_2$, was prepared in a similar manner; it crystallises in colourless plates or needles, and melts at 71°; its *hydrobromide*, $C_{18}H_{18}N_2 \cdot HBr$, forms colourless plates, melting at 221°. With nitrous acid, it yields a *mono-nitrosoamine*, $NO \cdot NEt \cdot C_{10}H_6 \cdot NHPh$, which crystallises in yellowish tables, melts at 145–146°, and gives Liebermann's reaction. With *acetic anhydride*, it yields an *anhydro-base*, $C_{10}H_6 < \begin{smallmatrix} NEt \\ | \\ NPh \end{smallmatrix} > CM_e \cdot OH$, which melts at 197–198°, and crystallises in short prisms. When heated at 100° with benzaldehyde, it yields a dihydroimidazole, $C_{10}H_6 < \begin{smallmatrix} NEt \\ | \\ NPh \end{smallmatrix} > CHPh$, which crystallises in colourless needles, melts at 108°, and is decomposed into its constituents on treating it with mineral acids.

Diphenyldihydrotoluinoxaline, $C_6H_3Me < \begin{smallmatrix} NH \cdot CHPh \\ | \\ N=CPh \end{smallmatrix} >$, melting at 143°, is obtained in yellow needles on heating 1 : 3 : 4-tolyleneorthodiamine with benzoïn at 180° under pressure, in addition to some of the diphenyltoluinoxaline of Hinsberg (Abstr., 1884, 1052), melting at 111°. The iron salt of the latter is readily formed when the dihydro-compound is oxidised by warming its alcoholic solution with ferric chloride.

Diphenyldihydronaphthaquinoxaline, is obtained in a similar manner from $\alpha\beta$ -naphthylenediamine, together with some of the diphenylnaphthaquinoxaline melting at 147° prepared by Lawson (Abstr., 1885, 1238). It is converted into the latter substance by oxidation with ferric chloride. It forms yellow crystals, and melts at 172°.

β -Ethylnaphthylenediamine can be prepared in the following manner:— β -Ethylnaphthylamine is converted into the *benzeneazo*-compound, $NHEt \cdot C_{10}H_6 \cdot N_2Ph$, which crystallises in dark red needles,

melting at 105° ; or, by treatment with paradiazobenzenesulphonic acid, into the compound $\text{NH} \cdot \text{Et} \cdot \text{C}_{10}\text{H}_6 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$. The latter, when reduced with zinc-dust and acetic acid, yields the diamine as a viscid, unstable oil; the *hydrochloride* forms colourless plates which easily turn red; the *platinochloride*, $(\text{C}_{12}\text{H}_{14}\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$, is a yellow, crystalline powder. With salicylaldehyde it yields an *anhydro-base*, $\text{C}_{10}\text{H}_6 \cdot \text{C} \begin{smallmatrix} \text{---} \text{C} \\ \text{N} \text{Et} \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, crystallising in yellowish-white prisms, and melting at 133° . With paranitrobenzaldehyde, an analogous *anhydro-base* is obtained in yellow needles melting at 225° .

1 : 3 : 4-*Methyltolylenediamine* was prepared by Gattermann's method (Abstr., 1885, 975). It is a very unstable substance; its *hydrochloride*, $\text{C}_8\text{H}_{12}\text{N}_2 \cdot \text{HCl}$, forms colourless plates melting at $175\text{--}180^{\circ}$; the *sulphate*, hygroscopic, deliquescent, colourless or reddish needles; the *picrate*, $\text{C}_8\text{H}_{12}\text{N}_2 \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$, small, yellow crystals melting at 164° ; and the *oxalate*, $\text{C}_8\text{H}_{12}\text{N}_2 \cdot \text{C}_2\text{H}_2\text{O}_4$, white needles melting at 124° . When boiled with formic acid, it yields *methenylparan-methyltolylenediamine*, $\text{C}_6\text{H}_3\text{Me} \cdot \text{C} \begin{smallmatrix} \text{---} \text{N} \\ \text{NMe} \end{smallmatrix} \text{CH}$ [$\text{Me} : \text{N} : \text{NMe} = 1 : 3 : 4$], as colourless needles melting at 94° . This is isomeric with the substance obtained by O. Fischer (Abstr., 1889, 731) from methenyltolyleneamidine and methyl iodide; Fischer's compound must have been $\text{C}_6\text{H}_3\text{Me} \cdot \text{C} \begin{smallmatrix} \text{---} \text{NMe} \\ \text{N} \end{smallmatrix} \text{CH}$ [$\text{Me} : \text{NMe} : \text{N} = 1 : 3 : 4$].

The *ethenyl* compound, $\text{C}_{10}\text{H}_{12}\text{N}_2$, was prepared in a similar manner, using acetic anhydride; it forms colourless needles melting at 142° , and is identical with the substance obtained by Niementowski (Abstr., 1887, 937) by reducing methylmetanitroparacetotoluidide with carbon bisulphide; the diamine yields a *thiocarbamide*, $\text{C}_6\text{H}_3\text{Me} \cdot \text{C} \begin{smallmatrix} \text{NH} \\ \text{NMe} \end{smallmatrix} \text{CS}$

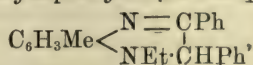
or $\text{C}_6\text{H}_3\text{Me} \cdot \text{C} \begin{smallmatrix} \text{---} \text{N} \\ \text{NMe} \end{smallmatrix} \text{C} \cdot \text{SH}$; this forms white needles, melts at 194° , and dissolves in alkalis. With benzaldehyde, the diamine yields

n-methylbenzenyltolyleneamidine, $\text{C}_6\text{H}_3\text{Me} \cdot \text{C} \begin{smallmatrix} \text{---} \text{N} \\ \text{NMe} \end{smallmatrix} \text{CPh}$, as colourless crystals melting at $126\text{--}127^{\circ}$; the *platinochloride*, $(\text{C}_{15}\text{H}_{14}\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$, forms brilliant, yellow needles melting above 300° . Orthonitrobenzaldehyde yields an analogous compound, $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_2$, as yellow crystals melting at $152\text{--}153^{\circ}$. Paranitrobenzaldehyde also yields an analogous compound, $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_2$, crystallising in brown needles. Salicylaldehyde yields a compound, $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}$, melting at 180° , and crystallising in white needles. Benzoin yields *n-methyldiphenyltoluidohydroquinoxaline*, $\text{C}_6\text{H}_3\text{Me} \cdot \text{C} \begin{smallmatrix} \text{N} = \text{CPh} \\ \text{NMe} \cdot \text{CHPh} \end{smallmatrix}$, melting at 135° . This,

when oxidised with ferric chloride, yields a yellow iron salt melting at 118° , but the base liberated from this could be obtained only as an uncrystallisable oil.

Parethylorthotolylenediamine, $\text{C}_6\text{H}_3\text{Me}(\text{NH} \cdot \text{Et}) \cdot \text{NH}_2$ [$= 1 : 4 : 3$], melting at 55° , has already been prepared by Gattermann (Abstr., 1885, 975). The *hydrochloride*, $\text{C}_9\text{H}_{14}\text{N}_2 \cdot \text{HCl}$, is a white substance melting at 176° ; the *oxalate*, $(\text{C}_9\text{H}_{14}\text{N}_2)_2 \cdot \text{C}_2\text{H}_2\text{O}_4$, forms white needles

melting at 151°. With carbon bisulphide, it yields a thiocarbamide, $C_6H_5Me < \begin{smallmatrix} -N \\ NEt \end{smallmatrix} > C \cdot SH$, which melts at 139°, crystallises in white, asbestos-like needles, and is soluble in alkalis. With acetic anhydride, it yields *ethenylethyltolylenediamine*, $C_6H_5Me < \begin{smallmatrix} -N \\ NEt \end{smallmatrix} > CMe$, in colourless crystals melting at 165–166°. The isomeric substance melting at 93°, obtained by Hübner (Abstr., 1882, 503) by ethylating ethenyltolyleneamidine, must have been $C_6H_5Me < \begin{smallmatrix} NEt \\ -N \end{smallmatrix} > CMe$ [Me : NEt : N = 1 : 3 : 4]. Benzaldehyde with the diamine yields the compound $C_6H_5Me < \begin{smallmatrix} -N \\ NEt \end{smallmatrix} > CPh$, as yellow needles; its *platinochloride*, $(C_{16}H_{16}N_2)_2 \cdot H_2PtCl_6$, forms yellow plates. Orthonitrobenzaldehyde yields an analogous compound, $C_{16}H_{16}N_3O_2$, as yellow crystals melting at 170°. Paranitrobenzaldehyde yields a benzylidene compound $NHEt \cdot C_6H_5Me \cdot N : CH \cdot C_6H_4 \cdot NO_2$, as red needles; these, when crystallised from alcohol, become converted, by gradual oxidation, into yellow needles, consisting of a compound, $C_{16}H_{15}N_3O_2$, corresponding with that obtained from orthonitrobenzaldehyde; it melts at 176°. Salicylaldehyde also yields a similar compound, $NHEt \cdot C_6H_5Me \cdot N : CH \cdot C_6H_4 \cdot OH$, as yellow needles melting at 78°, and convertible, by oxidation with mercury oxide, into the anhydro-base; this forms colourless crystals, and melts at 112–116°. With benzoïn, the diamine yields *n-ethylidiphenyldihydrodrotoluquinoxaline*,



in yellow crystals melting at 129°. When oxidised with ferric chloride, this substance yields an iron salt which crystallises in yellow needles, and melts at 155–160°. The base liberated from the iron salt was an uncrystallisable oil.

C. F. B.

Constitution of Nicotine. By A. PINNER (*Ber.*, 26, 292–305; see also Abstr., 1892, 1497).—A further examination of the two compounds obtained by the action of bromine on nicotine shows that they have the compositions $C_{10}H_{10}N_2Br_2O$ and $C_{10}H_8N_2Br_2O_2$. The author names these compounds dibromocotinine and dibromoticonine respectively.

Dibromocotinine is obtained as perbromide, $C_{10}H_{10}N_2Br_2O \cdot HBr_3$, by adding bromine to an aqueous solution of nicotine hydrobromide. The free base is best prepared by treating the perbromide with aqueous sulphurous acid, and then adding potassium carbonate. It crystallises from dilute alcohol in beautiful colourless prisms, melts under boiling water, but when dry it melts at 125°. The *hydrochloride* crystallises in needles, and turns blue on heating. The *methiodide*, $C_{10}H_{10}N_2Br_2O \cdot MeI$, crystallises in beautiful prisms, and melts at 175° with decomposition. Neither a benzoyl nor acetyl compound could be obtained. Hydroxylamine and phenylhydrazine are without action at low temperatures, and at higher temperatures complete decomposition ensues. When heated with sulphurous and sulphuric

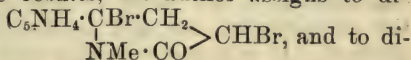
acids at 130–140°, or with sodium sulphite and fuming hydrochloric acid at 150°, it yields methylamine, oxalic acid, and β -methyl pyridyl ketone. The latter yields a platinochloride, C_7NH_7O, H_2PtCl_6 , which crystallises in flat, yellowish-red needles, and melts at 193° with decomposition.

Cotinine, $C_{10}N_2H_{12}O$, is obtained, together with a small quantity of nicotine, by reducing the above perbromide with zinc-dust and hydrochloric acid. It melts at 50°, distils as a colourless oil at 330° under the ordinary pressure, and at 250° under 150 mm. It is extremely stable, and is not altered by heating with baryta or with hydrochloric acid at 180°. The *platinochloride* crystallises in beautiful, yellowish-red prisms, and melts at 220° with carbonisation.

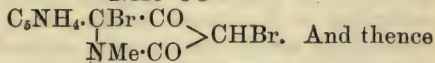
Dibromoticonine.—The *hydrochloride* crystallises in colourless needles, and blackens above 200° without melting. The *platinochloride* crystallises in yellow prisms, begins to darken at 230°, sinters at 240°, and does not melt at 250°. The *picrate* crystallises in small, yellow needles, turns brown at 220°, and melts at 235° with violent decomposition. Dibromoticonine, when reduced in cold alkaline solution with zinc-dust, yields monobromoticonine; in a warm alkaline solution, however, it yields methylamine and pyridyl- $\beta\gamma$ -dihydroxybutyric acid, $C_5NH_4[CH\cdot OH]_2\cdot CH_2\cdot COOH$. When heated with barium hydroxide in a sealed tube at 100°, it yields methylamine, nicotinic acid, and malonic acid.

Bromoticonine, $C_{10}H_9N_2BrO_2$, is obtained in small rhombohedra, and is easily soluble in alcohol. The *hydrochloride* forms small prismatic crystals, and when heated decomposes without melting.

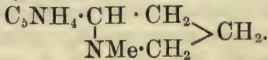
In consideration of the above results, the author assigns to dibromocotinine the constitution



bromoticonine the constitution



deduces for nicotine the constitution



E. C. R.

Oxidation of Strychnine. By J. TAFEL (*Ber.*, 26, 333–335; compare *Abstr.*, 1890, 1447; 1891, 1262; 1892, 1012).—By successive treatment of strychnine with dilute and concentrated nitric acid, the author has succeeded in obtaining a series of crystalline, well characterised acids, one of which has the composition $C_{10}H_5N_3O_8$, and contains the carboxyl group, two nitro-groups, and two hydroxyl groups; its formula may, therefore, be resolved as follows: $C_9H_2N(NO_2)_2(OH)_2\cdot COOH$. Such an acid must in all probability be a derivative of quinoline or isoquinoline, and it is hoped that the further examination of this and the other acids mentioned above will lead to important conclusions with regard to the constitution of strychnine.

H. G. C.

Pseudopelletierine. By G. CIAMICIAN and P. SILBER (*Ber.*, 26, 156–159; compare *Abstr.*, 1892, 1110).—*Pseudopelletierine oxime*, $C_9H_{16}N_2O$, is formed on treating an aqueous solution of the base

with hydroxylamine; it crystallises in colourless, rhombic plates melting at 128—129°. The *hydrochloride*, $C_9H_{16}N_2O \cdot HCl$, forms well-defined crystals, and volatilises when heated, but without melting.

A *base*, which seems to have the composition $C_9H_{17}NO$, is produced, together with a very small quantity of a crystalline substance melting at 240—260°, when pseudopelletierine is reduced with sodium amalgam in aqueous solution; it can be isolated in the form of its *aurochloride*, $C_9H_{17}NO \cdot HAuCl_4$, which crystallises in yellow needles melting at 203°.

When pseudopelletierine methiodide (*loc. cit.*) is heated with a solution of barium hydroxide, it is decomposed into dimethylamine and a colourless oil of the composition $C_8H_{10}O$, which boils at 197—198°; the latter is possibly a dihydroacetophenone, as, on oxidation with alkaline potassium permanganate, it yields phenylglyoxylic acid, and a small quantity of another acid which, however, was not obtained in a state of purity.

A compound of the composition $C_9H_{12}BrNO_2$ is formed when pseudopelletierine hydrobromide is treated with excess of bromine; it crystallises in long needles, melts at 207°, and is soluble in acids and alkalis, but only sparingly in hot water.

F. S. K.

Amyloid Substance. By N. P. KRAWKOW (*Bied. Centr.*, **21**, 753—754; from *Centr. Med., Wiss.*, 1892, 145—148).—Amyloid gives the characteristic carbohydrate reaction with iodine, notwithstanding its proteid nature. It differs from all other known products of degeneration in not being present in the organism in any phase of the physiological life, and is therefore looked on as a pathological product. It is now shown that chitin, $C_{60}H_{100}N_8O_{28} + nH_2O$ (which according to Sundwick is the amine derivative of a carbohydrate, $C_{60}H_{100}O_{50}$), which occurs very extensively in the animal kingdom, gives the characteristic reactions of amyloid.

Chitin was prepared by extracting crab's shell with dilute hydrochloric acid, boiling with 5 per cent. aqueous potash, decolorising with permanganate, and after making slightly acid, extracting with alcohol and ether. The colourless plates so obtained gave an intense red-brown coloration with iodine, which changed to violet on the addition of sulphuric acid or zinc chloride. Methyl-violet colours chitin violet-red or violet. Chitin plates kept in the abdominal cavity of a dog for two or three weeks gave a more distinct reaction with methyl-violet; keeping in the lymph cavity of a frog had no effect. The examination of several chitin formations (of crabs, cockroaches, spiders, &c.), showed that the chitin is not everywhere the same. The horny, inner wall of a bird's crop, which is also possibly chitin, gave the iodine reaction and (very feebly) the methyl-violet reaction. Chitin is produced in normal life, not only in the lower, but also in some higher animals.

N. H. M.

Organic Chemistry.

Combination of Cuprous Cyanide with Alkali Cyanides. By E. FLEURENT (*Compt. rend.*, 116, 190—191).—The colourless solution from which the blue and green ammoniocupric compounds previously described (Abstr., 1892, 1065) have separated, quickly deposits plates with a micaceous lustre, and afterwards, when the solution has become concentrated by spontaneous evaporation, prismatic crystals separate. The micaceous plates are *diammonio-cuprous diammonium cyanide*; this is insoluble in cold water, but is decomposed by boiling water with evolution of ammonia and precipitation of cuprous cyanide, and by acids with liberation of hydrogen cyanide and separation of cuprous cyanide. It is soluble in ammonia, and the solution rapidly becomes blue. When heated, the compound decomposes with liberation of water, ammonia, and ammonium cyanide, a residue of cuprous cyanide and metallic copper being left.

The prismatic crystals are *potassium cuprous cyanide*, $\text{Cu}_2\text{Cy}_2 \cdot 2\text{KCy}$, and consist of rhombic prisms truncated by pyramids. They are insoluble in, but are partially decomposed by, cold water, and are decomposed by boiling water, yielding cuprous and potassium cyanides. The compound dissolves in ammonia, forming a blue solution, and is decomposed by acids and by the action of heat.

C. H. B.

Tribromacetonitrile. By C. BROCHE (*J. pr. Chem.* [2], 47, 304).—*Tribromacetonitrile*, $\text{CBr}_3\cdot\text{CN}$, is obtained by distilling tribromacetamide with phosphorus pentoxide; it is a red, heavy, refractive liquid, boils undecomposed at 170° , and has the characteristic nitrile odour. Hydrogen bromide does not polymerise this nitrile (compare Tscherwen-Iwanoff, Abstr., 1891, 1332); by saturating it with hydrogen chloride it is solidified, after some days, into a compound which shows a molecular weight by the cryoscopic method corresponding with $(\text{CBr}_3\cdot\text{CN})_3$; this crystallises in long, slender needles, and melts at $129\text{--}130^\circ$. The matter is being further investigated.

A. G. B.

Reactions of Ferric Salts with Thiocyanates. By J. H. GLADSTONE (*Chem. News*, 67, 1—3).—The author comments on H. M. Vernon's communication (this vol., i, 122), draws attention to certain misconceptions of his own work on the subject contained therein, indicates some probable causes of the variation of certain of that author's views from his own views, and finally expresses the opinion that, without discussing the theoretical conclusions, it would seem that Vernon's experiments are not only in accordance with his own views, but furnish some additional arguments in their favour. In the paper under comment, there is an assumption "that ferric chloride and potassic thiocyanate, in equivalent quantities, react almost completely at infinite concentration to form ferric thio-

cyanate;" this is apparently based on a comparison made with ferric thiocyanate prepared by decomposing barium thiocyanate by ferric sulphate. It is now shown that the ferric thiocyanate prepared in this manner is impure and not suitable for such comparison; the author is therefore still of opinion that there is no reason to suppose that in the mixture referred to, the ordinary law of reciprocal decomposition and the usual effect of increased mass do not hold good. Then, with reference to the effect of change of temperature on these reactions, the author points out that he showed, in his paper, "On the Effect of Heat on the Colour of Salts in Solution," (*Phil. Mag.*, 1857), that ferric chloride passes from orange to a deep and almost pure red. He now demonstrates that the amount of change varies greatly with the proportion of water present, and the length of time during which the heating is continued. Thus, in a 3.8 per cent. solution, the depth of colour was about doubled, whilst in a 0.06 per cent. solution, it was increased fourfold when heated from 20° to 60°; again a twentyfold increase of colour is observed when 1 equivalent of potassium thiocyanate is added to a solution containing 100 equivalents of ferric chloride at the ordinary temperature, but when the two are compared at 60°, the increase is not nearly so great. A weakening in colour on heating is also observed in a solution of the impure ferric thiocyanate prepared from barium thiocyanate and ferric sulphate, and in a solution containing 1 equivalent of ferric chloride to 100 equivalents of potassium thiocyanate; in fact the reduction in colour in this last case by heating from 20° to 60° amounted to 50 per cent. This result the author regards as curious, as it indicates that the action of increased temperature on ferric thiocyanate is analogous to that of increased dilution, whereas, in all solutions of coloured salts examined by him in 1857, the reverse was the case.

D. A. L.

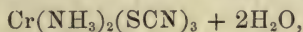
Reactions of Ferric Salts with Thiocyanates. By H. M. VERNON (*Chem. News*, 67, 66; compare this vol., i, 122, and preceding abstract).—Referring to the comments in the preceding abstract, the author points out that, in the ferric chloride and potassium thiocyanate reaction, there are present in solution potassium chloride and ferric thiocyanate, and that the barium thiocyanate and ferric sulphate experiment merely shows that the removal of one reacting salt from the solution produced practically no increase of colour. The author is, moreover, of opinion that only a small part of the change on heating ferric thiocyanate solutions is due to ferric chloride, and therefore, that the ferric thiocyanate solutions, under suitable conditions, increase in colour effect on heating, and so conform with the observation made by Gladstone in 1857 on solutions of other coloured salts.

D. A. L.

Thiocyanates of certain Chromammonium Compounds. By O. NORDENSKJÖLD (*Zeit. anorg. Chem.*, 1, 126—143).—Morland (this Journal, 13, 252) obtained a compound by the action of potassium dichromate on fused potassium thiocyanate; it was subsequently examined by Reinecke (*Annalen*, 126, 113). The author finds that it is best prepared by heating ammonium thiocyanate to

incipient fusion, and dropping in one-third its weight of ammonium dichromate; it is also obtained by adding 25 per cent. ammonia to a fused mixture of chromium thiocyanate and ammonium thiocyanate. The results described below show that it is an ammonium salt; its composition is represented by the formula $\text{Cr}(\text{NH}_3)_2(\text{SCN})_4\text{NH}_4$. It forms small, red crystals, is fairly stable towards acids, but is decomposed by alkalis; the corresponding *potassium* salt, $\text{Cr}(\text{NH}_3)_2(\text{SCN})_4\text{K}$, is obtained by adding potassium chloride to its solution. Both salts combine with 1 atom of iodine. The *barium*, *ferric*, *mercuric*, *silver*, *aniline*, and *piperidine* salts were also prepared. A reddish-yellow compound, $\text{Cr}(\text{NH}_3)_2(\text{SCN})_3(\text{HgS})_6$, separates when the mercuric salt is treated with hydrogen sulphide, whilst the *acid*, $\text{Cr}(\text{NH}_3)_2(\text{SCN})_4\text{H} + \text{H}_2\text{O}$, is isolated from the filtrate, and is also obtained by decomposing the barium salt with sulphuric acid; it commences to decompose at 80° .

When the above-described ammonium salt is boiled with hydrogen peroxide, hydrogen cyanide is evolved and a *compound*,



crystallising in large, purple, six-sided tables is obtained. It is only decomposed when treated with concentrated alkali, and when aniline, piperidine, or ethylenediamine is added to its solution, 1 or 2 mols. of water are displaced by residues of these bases.

A. R. L.

Hydrates of Alcohols. By R. DE FORCRAND (*Ann. Chim. Phys.* [6], 27, 525—549).—From numerous measurements of the heat generated on mixing aqueous solutions of isopropyl alcohol of different concentrations with a large volume of water, the author concludes that the alcohol forms two hydrates, of the composition $2\text{C}_3\text{H}_8\text{O}, \text{H}_2\text{O}$ and $\text{C}_3\text{H}_8\text{O}, 4\text{H}_2\text{O}$ respectively, but no evidence of the existence of other hydrates was obtained. From an examination of the results obtained by Dupré and Page, it would seem that methyl and ethyl alcohols form hydrates of the composition $\text{CH}_4\text{O}, 2\text{H}_2\text{O}$ and $\text{C}_2\text{H}_6\text{O}, 6\text{H}_2\text{O}$ respectively.

F. S. K.

Adonitol, a new Pentitol. By E. FISCHER (*Ber.*, 26, 633—639).—The annual report for 1892 issued by Merck, of Darmstadt, contains a description of a crystalline pentahydric alcohol obtained from *Adonis vernalis*, and named *adonitol*; this alcohol has now been examined by the author, who gives in the present paper the results of his own experiments, as well as Merck's description of the properties of the substance.

Adonitol, $\text{C}_5\text{H}_{12}\text{O}_6$, is very readily soluble in water, from which it crystallises in large, transparent prisms; the solution has at first a sweet taste, but this impression soon passes away, the tongue being left with a certain dull sensation; it is insoluble in ether and light petroleum, but dissolves freely in hot alcohol, being deposited from the solution on cooling in colourless needles. It begins to sinter at 99° , melts at 102° , and undergoes a slight increase in weight on prolonged heating at 105 — 115° , probably the result of absorption of oxygen; it does not reduce Fehling's solution, gives no coloration with aqueous alkalis, and dissolves in warm concentrated sulphuric

acid yielding a colourless solution; it is optically inactive, and has no specific physiological action.

When adonitol is oxidised with a cold dilute solution of sodium hypobromite, it is converted into a sugar, which, however, was not isolated. The *osazone*, $C_5H_5O_3(N_2HPh)_2$, prepared by treating the solution of this sugar with phenylhydrazine and acetic acid in the usual manner, separates from boiling water in yellow crystals, begins to sinter at 140° , and melts completely at 147° ; it is very similar in properties to l-arabinosazone, and, as will be shown below, it is very closely related to this substance.

Dibenzyladonitol, $C_5H_8O_3(CHPh)_2$, is formed when adonitol is treated with benzaldehyde and 50 per cent. sulphuric acid; it separates from hot alcohol in slender needles, melts at $164\text{--}165^\circ$ (uncorr.), is only very sparingly soluble in hot water, and is decomposed into adonitol and benzaldehyde by boiling 5 per cent. sulphuric acid.

The results described above prove that adonitol is isomeric with l-arabitol and xylitol, the only pentahydric alcohols known: xylitol has not yet been obtained in crystals, but adonitol and l-arabitol are not only similar in crystalline form and in solubility, but they have also the same melting point, and are both optically inactive in aqueous solution. Although so similar in general properties that they might be supposed to be identical, their aqueous solutions show a different optical behaviour in presence of borax, that of arabitol becoming fairly strongly laevorotatory, that of adonitol remaining inactive. The inference that adonitol is the inactive racemic modification of arabitol, although apparently well founded, is, however, negated by the fact that adonitol yields a crystalline, whereas arabitol gives an oily, benzal derivative. It would seem, therefore, that adonitol is not directly related to either of the known isomerides; assuming, further, that it contains a normal chain of carbon atoms, its configuration

must be represented by the formula

$$\begin{array}{ccccccc} & & H & & H & & H \\ & & | & & | & & | \\ OH \cdot CH_2 \cdot & C & - & C & - & C & \cdot CH_2 \cdot OH, \\ & | & & | & & | \\ & OH & & OH & & OH \end{array}$$

that is to say, it is the alcohol of ribose.

This view was proved to be correct; the pentahydric alcohol obtained by reducing ribonic lactone (Abstr., 1892, 437) with sodium amalgam is identical with adonitol.

Adonitol is the first pentitol that has been discovered in the vegetable kingdom, and the very fact of its occurrence renders it probable that ribose or its optical isomeride will also be met with in nature; judging from the experience gained in the reduction of mucic acid, there can be no doubt that all adonitol derivatives the molecules of which are asymmetric will be racemic modifications, as, for example, is so in the case of the osazone, which must be regarded as the racemic modification of arabinosazone.

F. S. K.

Dextrose. By A. WOHL (*Ber.*, 26, 730—744).—The oxime of dextrose, when treated with acetic anhydride, yields an acetyl derivative from which hydrogen cyanide can be eliminated, and on hydrolysis of the resulting compound a pentose is obtained. By repeating

this operation, the author hopes to prepare the series of compounds from dextrose to formaldehyde.

The *glucose oxime* is obtained as follows:—A solution of sodium in absolute alcohol is added to an aqueous solution of hydroxylamine hydrochloride in such proportions that phenolphthaleïn is no longer turned red. The mixture is filtered, heated to boiling, and then finely-powdered pure dextrose is added. On allowing the mixture to remain in a warm place for a few days, pure crystals of the oxime are deposited. It melts at 137.5° , and yields a stable hexacetyl derivative (m. p. $109-110^{\circ}$) and an unstable pentacetyl derivative.

Pentacetylglucononitrile is obtained by warming the oxime with fused sodium acetate and acetic anhydride: the product is poured into cold water, alkali added until the mixture is only faintly acid, and the precipitate crystallised from alcohol. It melts at $80-81^{\circ}$, and forms hemihedral crystals belonging to the rhombic system, $a : b : c = 0.66817 : 1 : 0.61841$. When hydrolysed with hydrochloric acid and treated with phenylhydrazine, it yields gluconic phenylhydrazide, m. p. $195-197^{\circ}$. When warmed with potassium hydroxide or treated with silver nitrate or ammoniacal silver solution, hydrogen cyanide is eliminated, and a pentose derivative is obtained. The alcoholic solution of the nitrile is treated with a solution of silver oxide in ammonia from which the excess of ammonia has been removed, and after the mixture has remained for some hours, the filtrate is freed from silver by means of hydrogen sulphide, and evaporated to a syrup. On hydrolysis, this syrup yields a mixture containing the pentose, which, however, is not obtained crystalline by this method. The *pentosazone* is, however, easily obtained from the mixture, and melts at $159-160^{\circ}$.

An *acetamide derivative* of the pentose,



is formed when the syrup obtained by the elimination of hydrogen cyanide from the above nitrile is allowed to remain two days with 30 per cent. ammonia. It may be prepared directly from the nitrile by allowing it to remain two days with silver oxide and excess of ammonia, and then heating the mixture on the water-bath, and, after driving off the ammonia with a current of air, concentrating the filtrate under diminished pressure. It crystallises in slender, white needles, has a sweet taste, is soluble in 25 parts of hot and 100 parts of cold 90 per cent. alcohol, and has a specific rotatory power $[\alpha]_{\text{D}}^{20} = -9.5^{\circ}$. When heated with dilute hydrochloric or sulphuric acid on the water-bath, it yields the pentose and acetamide.

The pentose *d.-arabinose* is obtained by heating the preceding compound (10 grams) with 50 c.c. of 6N sulphuric acid for 15 minutes on the water-bath. The cold solution is extracted with ether, which removes the acetic acid produced during the reaction. The acid solution is then exactly neutralised with barium hydroxide, and the filtrate, after boiling in a porcelain dish to remove the ammonia, is evaporated in a vacuum or on the water-bath to a syrup. *d.-Arabinose* tastes sweet, and crystallises in long, colourless prisms,

in the rhombic system, $a : b : c = 0.66810 : 1 : 0.48989$. The specific rotatory power is $[\alpha]_D^{20} = -104.1^\circ$. It yields furfuraldehyde with strong acids, is coloured yellow by alkalis, reduces Fehling's solution, and yields the osazone $C_5H_8O_3(N_2HPh)_2$ with phenylhydrazine, and the hydrazone $C_5H_{10}O_4 \cdot N_2H \cdot C_6H_4Br$ with bromophenylhydrazine.

i.-Arabinose is obtained by mixing solutions of the optical antipodes, and crystallises in microscopic needles. The osazone melts at 163° .

l.-Arabinose, when treated in a similar way to that described above for dextrose, is converted into a tetrose derivative.

l.-Arabinose oxime melts at $132-133^\circ$, and yields hydrocyanic acid when melted with an alkali. Tetracetyl arabinonitrile melts at $117-118^\circ$, and, when treated with ammoniacal silver solution, yields a tetrose derivative.
E. C. R.

Xylose. By W. E. STONE and W. H. TEST (*Amer. Chem. J.*, **15**, 195-197).—Xylose is conveniently obtained from the alkaline waste liquor which results from the digestion of straw with lime at a high temperature in the paper manufacture. The liquor contains, among other compounds, xylan, the mother substance of xylose, and this is precipitated by alcohol from the concentrated and acidified liquor, and purified by repeated solution in water and reprecipitation with alcohol. The yield of crude xylan is about 1 per cent. It still contains, however, a considerable amount of lime salts, and yields, on distillation with hydrochloric acid, about 46 per cent. of furfuraldehyde, as determined by titration with phenylhydrazine. The xylan is hydrolysed with dilute sulphuric acid, and the resulting solution of xylose neutralised, evaporated to a syrup, and extracted with alcohol. The alcoholic extract yields a syrup of xylose, which soon crystallises, and is identified by its specific rotatory power $[\alpha]_D = 18.4^\circ$, and the melting point, 158° , of its lævorotatory osazone. The straw liquor may be hydrolysed directly without the intermediate separation of the xylan, and with equally good results. The authors confirm the observations of Tollens and Parcus (*Abstr.*, 1890, 1084) as to the multirotation of xylose. The specific rotatory power in aqueous solution diminished in the course of three hours from $[\alpha]_D = 71.65^\circ$ to 18.95° , and eventually became constant at 18.40° .

JN. W.

Gum Arabic. By A. BÉCHAMP (*Bull. Soc. Chim.* [3], **7**, 587-600).—The so-called nitro-derivatives of arabin, like those of starch and cellulose, are nitrates. Arabin mononitrate has a rotatory power in alcoholic solution $[\alpha]_D = 23.2-28.2^\circ$, and arabin dinitrate a rotatory power $[\alpha]_D = 22.56^\circ$, whilst arabin itself is lævorotatory, the author having previously fixed its rotatory power at about -36° . In view, however, of the somewhat conflicting statements of other chemists, he has re-determined the constant.

The raw material employed was Senegal gum, which was dried at 130° . Arabin prepared from the latter, either by treatment with hydrochloric acid (Fremy's method) or with sodium hydroxide, exhibits a low rotation when the action of these reagents is protracted. The following method appears to be the most satisfactory ;

—Glacial acetic acid is added to a thick mulcilage of the gum, the filtered liquid mixed with a larger quantity of glacial acetic acid, and the precipitate collected and washed with fresh quantities of the same acid; it is then redissolved in water, precipitated with a large excess of alcohol, collected, and dried over concentrated sulphuric acid. The arabin thus prepared contains 0.5 per cent. of ash, and has a rotatory power $[\alpha]_D = -35^\circ$. After being heated for some time at 130° , it gives a lower rotation and dissolves in water with a yellow colour. An aqueous solution containing 5—7 per cent. may be mixed with an equal volume of alcohol of 94° without precipitation; the whole of the arabin is, however, precipitated on the addition of a small quantity of ammonium acetate. The author shows that a solution of the gum itself is lævorotatory, like that of the arabin, and solutions of both give a bluish precipitate with Fehling's solution, which dissolves on heating. A solution of arabin becomes dextrorotatory on being heated in a sealed tube at 160° ; the product reduces Fehling's solution, and its acid reaction becomes much stronger.

When to a mulcilage of the gum three-fourths the weight of ordinary nitric acid is added in the cold, a similar effect is observed to that produced by hydrochloric or sulphuric acid, namely, the lævorotation becomes a dextrorotation. If, however, the gum is dissolved in a mixture of nitric acid (36° B., 3 parts) and water (1 part), and the solution heated, mucic acid (12—15 per cent.) is formed, the filtrate being lævorotatory. The last-mentioned rotation diminishes, however, on continuing the action, and oxalic acid is produced; the author is therefore inclined to agree with Dubrunfaut, that gum contains both dextro- and lævo-components. A. R. L.

Oxycellulose and Bornesitol. By E. R. FLINT and B. TOLLENS (*Annalen*, **272**, 288—290).—Analyses of fresh preparations of oxycellulose have given results agreeing very closely with those obtained by Sacc, and moderately well with those of Lindsey and Tollens (Abstr., 1892, 827) and of Cross and Bevan (Trans., 1883, 22); oxycellulose does not yield methylic iodide when heated with hydriodic acid, and, judging from its reactions, it would seem to contain aldehyde groups.

A yellowish, crystalline compound obtained from the water used in washing caoutchouc was purified and examined by the authors, and found to be bornesitol, or methylinositol, $C_7H_{14}O_6$; it melted at 199 — 203° , had a specific rotatory power $[\alpha]_D = +31.16^\circ$, and gave, on treatment with hydriodic acid, a quantity of methylic iodide corresponding with the presence of one methoxy-group. F. S. K.

Explosive Nitrates from the Jute Fibre. By C. F. CROSS and E. J. BEVAN (*J. Soc. Chem. Ind.*, **11**, 214—215).—The authors criticise a communication by Mülhåuser (*Dingl. polyt. J.*, **283**, 88) on the jute fibre as a raw material for gun-cotton, which they consider to lack in novelty, most of the facts having been previously described by them (Trans., 1889, 202). D. B.

Chlorine Derivatives of Propylamines, Benzylamines, Aniline, and Paratoluidine. By A. BERG (*Compt. rend.*, 116, 327—329).—The author uses the terms chloramine and dichloramine to distinguish those compounds in which the halogen replaces the hydrogen in the amido-group, and not in the hydrocarbon group.

Propylchloramine, NHPrCl , is obtained by mixing solutions of propylamine hydrochloride and sodium hypochlorite. It is a colourless liquid with a very piquant odour; sp. gr. at $0^\circ = 1.021$, but at 15° it is lighter than water at the same temperature. It does not solidify at -50° , and cannot be distilled, because it decomposes very rapidly when gently heated. Decomposition takes place after a little time, even at the ordinary temperature. With sulphuric acid, it yields propylamine and the dichlor-derivative.

Propyldichloramine, NPrCl_2 , is easily obtained by the method that Tcherniac employed for the preparation of ethyldichloramine. It is a greenish-yellow liquid, with an odour similar to that of other dichloro-derivatives. It does not solidify at -50° , and boils without decomposition at 117° under a pressure of 760 mm.; sp. gr. at $0^\circ = 1.177$.

Dipropylchloramine, NPr_2Cl , is obtained by the action of sodium hypochlorite on dipropylamine hydrochloride. It is a colourless, oily liquid, insoluble in water, and decomposes slowly with precipitation of crystals; sp. gr. at $0^\circ = 0.923$. It boils at 143° under a pressure of 771 mm., and when treated with alcoholic soda, yields a base that seems to be propylpropylidenamine. When mixed with an alcoholic solution of potassium cyanide, a reaction takes place at the ordinary temperature with development of heat, the product being dipropylcyanamide, identical with that obtained by Chancel by another method (following abstract).

Benzylchloramine, $\text{C}_7\text{H}_7\cdot\text{NHCl}$, is obtained in a similar manner. It is a colourless, very unstable liquid, which decomposes very rapidly with deposition of crystals and evolution of thick, white fumes.

Benzyldichloramine, $\text{C}_7\text{H}_7\cdot\text{NCl}_2$, cannot be obtained by the reaction used by Tcherniac in the case of ethyldichloramine, but is easily obtained by treating rapidly washed benzylchloramine first with dilute sulphuric acid and then with acid gradually increasing in concentration until it reaches 50 to 60 per cent. Benzyldichloramine is a greenish-yellow liquid with a chlorous odour; sp. gr. at $0^\circ = 1.282$. When cooled, it solidifies to greenish-yellow, striated prisms which melt at -11.5° ; it cannot be distilled, even in a vacuum.

Dibenzylchloramine, $\text{N}(\text{C}_7\text{H}_7)_2\text{Cl}$, is obtained by the action of sodium hypochlorite on dibenzylamine hydrochloride. It crystallises from ether in large, lozenge-shaped crystals which seem to be flattened rhombohedra, and has an agreeable odour, recalling that of oil of bitter almonds, and only slightly chlorous. It is insoluble in water, and only slightly soluble in cold alcohol of 93° , but the solubility in the latter increases very rapidly as the temperature rises, the weight dissolved by 100 parts of alcohol being as follows:—

16°.	34°.	44°.	47.5°.	53°.
3.20	43.88	97.03	164.80	493.60

Dibenzylchloramine melts at 56° , and, if heated rapidly, deflagrates vigorously at 150° ; if heated more gradually, deflagration takes place at a lower temperature. At the ordinary temperature, decomposition takes place slowly, and the crystals become partially insoluble in ether. With potassium cyanide, dibenzyleyanamide is formed.

Aniline and paratoluidine yield similar products, which are extremely unstable and deflagrate rapidly a few minutes after the solvent (ether or ethylic chloride) has evaporated. C. H. B.

Dipropyleyanamide and Dipropylcarbodiimide. By F. CHANCEL (*Compt. rend.*, 116, 329—330) — *Dipropyleyanamide* is obtained by adding bromine water gradually to a saturated aqueous solution of dipropylamine containing half a molecular proportion of potassium cyanide, until the liquid is neutral: $2\text{NHPr}_2 + \text{KCN} + \text{Br}_2 = \text{NPr}_2\text{CN} + \text{NHPr}_2\text{HBr} + \text{KBr}$. It is a mobile liquid, with a burning taste and an aromatic odour, and boils at 107° under a pressure of 21 mm. and at 220° under 770 mm.; sp. gr. at $0^{\circ} = 0.88$. It is insoluble in water, but dissolves in alcohol and in ether, and, although neutral to litmus, dissolves readily in concentrated hydrochloric acid, and slightly in the dilute acid. The aurochloride is oily and insoluble. When heated with hydrochloric acid in sealed tubes at 150° , the cyanamide yields carbonic anhydride, ammonium chloride, and dipropylamine hydrochloride.

Dipropylcarbodiimide, $\text{NPr}_2\text{C}:\text{NPr}_2$, is obtained by gradually adding dry yellow mercuric oxide to a solution of symmetrical dipropylthiocarbamide in dry benzene until the liquid no longer gives a black precipitate with ammoniacal silver nitrate. It is a mobile liquid, with an odour and taste recalling that of its isomeride, dipropyleyanamide; sp. gr. at $0^{\circ} = 0.86$. It boils at 80° under a pressure of 28 mm. and at 171° under 765 mm., is insoluble in water, but dissolves in alcohol and in ether, and is easily decomposed by acids, even at the ordinary temperature, the products being symmetrical dipropylthiocarbamide if the acid is dilute, but if the acid is concentrated, hydrolysis proceeds further, and carbonic anhydride is given off. C. H. B.

Muscarine. By G. NOTHNAGEL (*Ber.*, 26, 801—806).—Certain compounds of a natural *muscarine*, from the *Fly agaric*; of artificial *muscarine*, obtained from choline by oxidation with nitric acid (Schmiedeberg and Harnack, *Chem. Centr.*, 1876, 558); and of *anhydromuscarine* (Berlinerblau, *Abstr.*, 1885, 1056; compare E. Fischer, this vol., i, 301), have been prepared, to ascertain how far they differ from each other; *isomuscarine* has been previously studied (Schmidt, *Abstr.*, 1892, 905; Bode, *ibid.*, 806). Anhydromuscarine differs from the others in composition, crystalline form of its platino-chloride and aurochloride, and in physiological action. Artificial muscarine and natural muscarine, on the other hand, are alike in crystalline form, in solubility, and composition of their platino- and auro-chlorides, and, to a large extent, in their physiological action. They differ, however, in that artificial muscarine induces paralysis of the intermuscular nerve-terminations in the frog, and myosis in the

pupil of the eyes of birds, whilst natural muscarine does neither of these things; the two substances are, perhaps, physically isomeric.

Acetyltrimethylammonium platinochloride,



forms long prisms, sometimes containing $1\text{H}_2\text{O}$; the *aurochloride* was also prepared. The base is converted by baryta-water into *anhydromuscarine*, the *platinochloride* of which, $(\text{NMe}_3\text{Cl}\cdot\text{CH}_2\cdot\text{CHO})_2\text{PtCl}_4$, forms orange-red, quadratic tables, the *aurochloride* yellow needles. Anhydromuscarine yields, with phenylhydrazine, an unstable hydr-azide.

Artificial *muscarine platinochloride*, $[\text{NMe}_3\text{Cl}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})_2]_2\text{PtCl}_4 + 2\text{H}_2\text{O}$, crystallises in octahedra, the *aurochloride* in yellow needles. Unlike choline, the base yields neither acetyl nor benzoyl derivatives; when treated either with acetic anhydride or with benzoic chloride, it yields a substance whose *platinochloride*, $(\text{NMe}_3\text{Cl}\cdot\text{CH}_2\cdot\text{CHO})_2\text{PtCl}_4$, melts at $228\text{--}229^\circ$, and crystallises in octahedra, and is quite different from that of anhydromuscarine. Besides artificial muscarine, *choline nitrite* is formed by the action of nitric acid on choline; its *platinochloride*, $(\text{NMe}_3\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{NO})_2\text{PtCl}_4$, melts at $223\text{--}224^\circ$, and the *aurochloride*, which forms yellow needles, at 240° ; the base gives Liebermann's nitroso-reaction.

Natural muscarine yields a *platinochloride*,

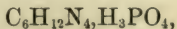


and an *aurochloride* identical in appearance with those of artificial muscarine. A third *platinochloride*, of similar appearance and composition, was obtained from a base formed by the prolonged action of sodium amalgam on an aqueous solution of betaine hydrochloride.

C. F. B.

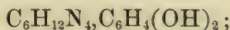
Additive Products and Compounds of Hexamethyleneamine.

By H. MOSCHATOS and B. TOLLENS (*Annalen*, 272, 271—288; compare Abstr., 1891, 663).—*Hexamethyleneamine phosphate*,



and the *tartrate*, $\text{C}_6\text{H}_{12}\text{N}_4, \text{C}_4\text{H}_6\text{O}_6$, are crystalline compounds, but the *citrate* is an oil; on adding copper sulphate to a concentrated aqueous solution of hexamethyleneamine, a greenish substance, of the composition $8\text{CuO}, 2\text{SO}_3 + 7\text{H}_2\text{O}$, is precipitated, whereas with lead nitrate, a basic salt, of the composition $\text{Pb}(\text{NO}_3)\cdot\text{OH}$, is formed.

Hexamethyleneamine combines with phenols in concentrated aqueous solution, yielding crystalline compounds which have, as a rule, no definite melting point; the following compounds were prepared:—*Hexamethyleneamine triphenol*, $\text{C}_6\text{H}_{12}\text{N}_4, 3\text{PhOH}$; *hexamethyleneamine dicatechol*, $\text{C}_6\text{H}_{12}\text{N}_4, 2\text{C}_6\text{H}_4(\text{OH})_2$; *hexamethyleneamine resorcinol*, $\text{C}_6\text{H}_{12}\text{N}_4, \text{C}_6\text{H}_4(\text{OH})_2$; *hexamethyleneamine quinol*,



hexamethyleneamine dipyrogallol, $\text{C}_6\text{H}_{12}\text{N}_4, 2\text{C}_6\text{H}_3(\text{OH})_3$; *hexamethylene-*

amine phloroglucinol, $C_6H_{12}N_4, C_6H_3(OH)_3$; *hexamethyleneamine eugenol*, $C_6H_{12}N_4, C_{10}H_{12}O_2$, and the picrate.

The molecular weight of hexamethyleneamine, determined by the cryoscopic method in glacial acetic acid solution, was found to be 121–127°, a result which agrees more closely with that required by the molecular formula $C_6H_{12}N_4$ than the previous determinations of Mayer and Tollens.

F. S. K.

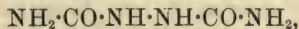
Isomerism of Asymmetrical Hydrazones. By A. CLAUS (*J. pr. Chem.* [2], 47, 267–273).—This is a discussion of Overton's paper on "Stereochemical Phenylhydrazones" (this vol., i, 208). Claus, as he has already frequently stated, cannot admit that any stereochemical theory is necessary.

A. G. B.

Hydrazine Derivatives. By T. CURTIUS (*Ber.*, 26, 403–410).—A preliminary account of a series of researches, which are to be described in full at a later date.

Primary acid hydrazines, $R \cdot CO \cdot NH \cdot NH_2$, are obtained by the action of hydrazine hydrate on the acid amide, chloride, or ethereal salt, best from the last-named. Derivatives were prepared from benzoic acid, nitro-, amido-, and hydroxy-benzoic acids, glycollic acid (this hydrazine was formerly described as hydrazineacetic acid, $N_2H_3 \cdot CH_2 \cdot COOH$), acetic, formic, hippuric, aceturic, $CMEO \cdot NH \cdot CO \cdot NH \cdot NH_2$, phthaluric, succinuric, and anilidoacetic acids. Also primary dihydrazines, $R''(CO \cdot NH \cdot NH_2)_2$, from succinic, malonic, oxalic, and fumaric acids. These primary hydrazines are colourless, solid, non-volatile substances; they crystallise well, and dissolve in water and alcohol, but not in ether. They form hydrochlorides, and the H of the NH group is replaceable by sodium or acetyl. They act as reducing agents, and with aldehydes and ketones condense to tertiary hydrazines.

Secondary acid hydrazines, $R \cdot CO \cdot NH \cdot NH \cdot CO \cdot R$, are obtained by heating the primary hydrazines; hydrazine is not evolved in the reaction to any extent, but is resolved into nitrogen and ammonia. The secondary hydrazines are very stable, insoluble, colourless substances; they melt at a high temperature, and react like acids. To this class must be reckoned phthalylhydrazine, $C_6H_4(CO)_2N_2H_2$, and



the product of the action of hydrazine hydrate on carbamide. Secondary dihydrazines, $R'' \begin{smallmatrix} CO \cdot NH \cdot NH \cdot CO \\ CO \cdot NH \cdot NH \cdot CO \end{smallmatrix} R''$, are obtained by the action of nitrous acid on primary dihydrazines.

Acid hydrazoides, $R \cdot CO \cdot N_3$, are obtained by the action of nitrous acid on the primary hydrazines of monobasic acids. When reduced, some yield acid hydrazines, for example, benzoylhydrazoide yields dibenzoylhydrazine, and, in an analogous manner, diazobenzenimide yields hydrazo- together with azo-benzene. When boiled for some time with water, benzoylhydrazoide loses nitrogen and carbonic acid, and a diamidobenzophenone is formed.

Certain other hydrazines, notably those of hippuric, aceturic, and fumaric acids, react differently with nitrous acid, and form compounds of the type $R \cdot CO \cdot NH \cdot N_2 \cdot OH$, or $R''(CO \cdot NH \cdot N_2 \cdot OH)_2$. When these

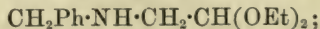
compounds are boiled with alcohol, nitrogen and water are lost, and compounds of the type $R \cdot CO \cdot NH \cdot OEt$ are formed.

The action of hydrazine hydrate on ethyl acetoacetate and benzoyl-acetate, and also on ethyl acetosuccinate and diacetosuccinate, has been studied; the resulting compounds appear to be derivatives of isopyrazolone. Pyrazoline itself, $C_3H_6N_2$, was obtained by the action of hydrazine hydrate on acetaldehyde; it is a volatile, readily oxidisable base, dissolves in water, and forms a well crystallised hydrochloride. By the action of hydrazine hydrate on the ethereal salts of γ -keto-acids, such as levulinic, β -benzoylpropionic, and β -benzoylisosuccinic acids, pyridazoone derivatives were finally obtained, hydrazine derivatives being usually formed as intermediate products. Benzoin yields first a hydrazine, $OH \cdot CHPh \cdot CPh \cdot N \cdot NH_2$, and this, when boiled with alcohol, loses ammonia and forms a ketazine, $CPhO \cdot CPh \cdot N \cdot N \cdot CPh \cdot CPhO$, which, with hydrazine hydrate, yields 2 mols. of diphenyltrihydrazimethylene, $N_2H_2 \cdot CPh \cdot CPh \cdot N_2H_2$.

Many inorganic double salts of hydrazine have been prepared, and found to resemble the corresponding ammonium salts. Salts of the type $(N_2H_4)_2H_2SO_4, R''SO_4$ were prepared in the case of $R'' = Cu, Ni, Co, Fe, Mn, Zn, Cd$; they are sparingly soluble. With NH_4, K, Na, Al, Mg , no such double sulphates were formed. Double chlorides of the type N_2H_4, HCl, RCl were obtained in the case of Hg, Cd, Zn, Fe , and Sn ; they are easily soluble, and some of them contain water of crystallisation. Magnesium hydrazine phosphate, analogous to the ammonium phosphate, has also been prepared. In general, hydrazine is thus seen to behave like a mon-acid base. The stable nitrate is N_2H_4, HNO_3 ; the other nitrate, $N_2H_4, 2HNO_3$, readily loses half its nitric acid. Free hydrazine is still unknown. C. F. B.

Amidacetaldehyde. By E. FISCHER (*Ber.*, **26**, 464—471; compare this vol., i, 187).—*Benzoylamidacetal*, $NHBz \cdot CH_2 \cdot CH(OEt)_2$, boils under a pressure of 15 mm. at $205-206^\circ$ (corr.), and decomposes when distilled at the ordinary pressure. Concentrated hydrochloric acid converts it into *hippuraldehyde*, $NHBz \cdot CH_2 \cdot COH$, which could not be isolated in the crystalline condition; the *hydrochloride* melts at $110-115^\circ$, and is converted into hippuric acid by means of bromine; the *phenylhydrazone* melts at $107-108^\circ$ (uncorr.).

Benzalamidacetal, $CHPh \cdot N \cdot CH_2 \cdot CH(OEt)_2$, obtained from benzaldehyde and amidacetal, is a colourless, highly refractive oil, boiling at 156° (corr.) under a pressure of 12 mm. When heated with dilute sulphuric acid, it yields *benzylamidacetal*,



this boils at 157° (corr.) under a pressure of 16 mm., and at the ordinary pressure between 280° and 290° with partial decomposition. It reduces Fehling's solution after boiling with an acid.

When amidacetal is treated with a mixture of methyl alcohol and methylic iodide, acetaltrimethylammonium iodide is obtained. The corresponding *chloride*, $NMe_3Cl \cdot CH_2 \cdot CH(OEt)_2$, which crystallises in needles, is prepared by shaking a solution of the iodide with silver chloride; concentrated hydrochloric acid converts it into the aldehyde,

$\text{NMe}_3\text{Cl}\cdot\text{CH}_2\cdot\text{COH}$. The *platinochloride* forms red, monoclinic crystals, $a : b : c = 0.7488 : 1 : 0.9906$; $\beta = 76^\circ 3' 39''$. The aldehyde base corresponding with this may, perhaps, be identical with muscarine.

A. R. L.

Molecular Weight of Metaldehyde. By F. ZECCHINI (*Gazzetta*, 22, ii, 586—592).—Hanriot and Oeconomides (*Abstr.*, 1882, 31), from determinations of the vapour density of metaldehyde, concluded that it should be represented as $(\text{C}_2\text{H}_4\text{O})_3$; these observers also stated that metaldehyde is almost wholly decomposed by boiling chloroform. This, however, the author finds does not hold for dilute solutions; the molecular formula, deduced from boiling point determinations of the most concentrated chloroform solutions (1.3—1.8 per cent.), which can be heated without the occurrence of sensible decomposition, is $(\text{C}_2\text{H}_4\text{O})_6$. Boiling point determinations of alcoholic solutions lead to molecular weights varying from 6 to 11 times that of aldehyde. Cryoscopic determinations of the molecular weight of metaldehyde dissolved in phenol agree fairly well with the formula $(\text{C}_2\text{H}_4\text{O})_4$, but are more in accordance with a molecular weight between three and four times that of aldehyde.

W. J. P.

Derivatives of Chloral. By A. BÉHAL and E. CHOAY (*Ann. Chim. Phys.* [6], 27, 319—339; compare *Abstr.*, 1890, 230 and 1093).—Chloral-ammonia very slowly decomposes at the ordinary temperature, the crystals being first converted into a liquid, which after some time separates into two layers, and deposits a crystalline substance. The upper stratum of liquid consists of an aqueous solution of ammonia and ammonium chloride; the lower one yields chloroform and chloraldiformamide on distillation from a water-bath; the crystalline deposit consists of chloraldiformamide and a little ammonium chloride.

Chloraldiformamide, $\text{C}_4\text{Cl}_3\text{H}_5\text{N}_2\text{O}_2$, melting at $216\text{—}217^\circ$, has been previously described (*loc. cit.*); when heated with concentrated hydrochloric acid, it is decomposed into chloral, ammonia, and formic acid; as, moreover, the compound can be synthesised by warming anhydrous chloral with formamide, its constitution may be expressed by the formula $\text{CCl}_3\cdot\text{CH}(\text{NH}\cdot\text{CHO})_2$, so that it is not a closed-chain compound, as previously supposed.

Chloralantipyrine, $\text{C}_{13}\text{H}_{15}\text{Cl}_3\text{N}_2\text{O}_3$, is formed when chloral hydrate is treated with phenylpyrazolone in aqueous solution; it is a crystalline substance, melts at $67\text{—}68^\circ$, and is moderately easily soluble in water (7.85 parts in 100 at 14°). Its aqueous solution gives a blood-red coloration with ferric chloride, reduces Fehling's solution on warming, and yields chloroform when boiled with potash; when the crystalline substance is heated at a temperature just above 100° , it is converted into a compound of the composition $\text{C}_{13}\text{H}_{13}\text{Cl}_3\text{N}_2\text{O}_2$, which forms small crystals melting at $186\text{—}187^\circ$, and insoluble in water. The *acetyl* derivative, $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{N}_2\text{O}_3$, prepared by heating chloralantipyrine with acetic anhydride and a trace of zinc chloride, separates from alcohol in crystals melting at $154\text{—}155^\circ$.

Dichloralantipyrine, $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}\cdot 2\text{C}_2\text{H}_3\text{Cl}_3\text{O}_2$, prepared in like manner, employing excess of chloral hydrate, melts at $67\text{—}68^\circ$, and its aqueous

solution gives a blood-red coloration with ferric chloride; 100 parts of water at 14° dissolve 9.98 parts of the substance.

The two compounds described above have a physiological action similar to that of chloral; although they contain such different quantities of the last-named substance, they have, weight for weight, equal toxic properties.

F. S. K.

Condensation of Chloral and Butylchloral with Acetone and Acetophenone. By W. KOENIGS and E. WAGSTAFFE (*Ber.*, 26, 554—559).—Koenigs has already shown (*Abstr.*, 1892, 694) that chloral unites with acetone and acetophenone to form aldol-like condensation products. The present paper gives the results of the further investigation of these substances, and of the compounds obtained in a similar manner from butylchloral.

Chloralacetone, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Ac}$, crystallises from light petroleum in rhombic pyramids, and forms an *oxime* which melts indefinitely between 95° and 105°. When chloralacetone is boiled for 10 minutes with a 4 per cent. solution of sodium carbonate, it is converted into β -acetylacrylic acid, $\text{CHAc}\cdot\text{CH}\cdot\text{COOH}$, which melts at 125—126°, and has all the properties assigned to it by Wolff (*Abstr.*, 1891, 1185). Owing to the ease with which it is decomposed by alkalis, the yield is not good, and is reduced to a minimum if 1 per cent. potash be employed instead of sodium carbonate.

Chloralacetophenone, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{COPh}$, separates from light petroleum in compact, monosymmetric crystals; unlike chloral or acetophenone, it has no hypnotic action. Its *oxime*, $\text{C}_{10}\text{H}_{10}\text{NCl}_3\text{O}_2$, crystallises from dilute alcohol in white scales melting at 135—137°, and the *hydrazone*, $\text{C}_{16}\text{H}_{15}\text{N}_2\text{Cl}_3\text{O}$, in yellowish crystals melting at 156—158°. With bromine, it yields a mixture of two *monobromo*-derivatives, which may be separated by fractional crystallisation from light petroleum, the more soluble derivative melting at 105°, and the less soluble at 152—153°. When carefully treated with boiling 1 per cent. potash, it is converted into *phenyl- γ -keto- α -hydroxybutyric acid*, $\text{COOH}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{COPh}$, which crystallises in white needles melting at 125—126°; the yield is small, as the alkali partially resolves it into acetophenone and oxalic acid. The *silver* salt is a white precipitate which may be recrystallised from hot water. When treated with pure sulphuric acid at 0°, the acid loses the elements of water, and is converted into β -benzoylacrylic acid, $\text{CHBz}\cdot\text{CH}\cdot\text{COOH}$, which crystallises from light petroleum in lustrous, yellow needles, and is identical with the benzoylacrylic acid obtained by Pechmann from maleic anhydride and benzene in presence of aluminium chloride (*Abstr.*, 1882, 1075). The *phenylketo- α -hydroxybutyric acid* recently prepared by Fischer and Stewart (*Abstr.*, 1892, 1448) is not identical with that obtained by the authors, and has, therefore, probably the constitution $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{COOH}$.

Butylchloral and acetophenone unite together when heated with an excess of acetic acid for 15—20 hours, and the resulting *butylchloralacetophenone*, $\text{CHMeCl}\cdot\text{CCl}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{COPh}$, which crystallises in white prisms, melts at 108—110°, and volatilises in a current of steam. When treated with pure sulphuric acid in the cold, it is converted

into *trichlorobutylideneacetophenone*, $\text{CHMeCl}\cdot\text{CCl}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{COPh}$, which crystallises from light petroleum in white plates, melts at $45\text{--}47^\circ$, and is also volatile in steam. H. G. C.

Chlorination of Acetone. By P. FRITSCH (*Ber.*, 26, 597—598).—The author finds that monochloroacetone, prepared by Barbaglia's process, is a somewhat complex mixture, a conclusion in agreement with that of Tcherniac (*Abstr.*, 1892, 1425). Even when chlorine is passed into acetone in quantity sufficient to convert only one-half of the ketone into its monochloro-derivative, the fraction of the product boiling at $119\text{--}120^\circ$ is impure, doubtless owing to the presence of mesityl oxide.

For the preparation of pure monochloroacetone, the following method is recommended:—The acetone is mixed with about one-third of its weight of marble, and, during chlorination, water is slowly dropped into the cooled liquid in order to dissolve the calcium chloride; the process is interrupted before the whole of the marble is dissolved, and the mixture is kept at a moderate temperature until the evolution of carbonic anhydride is at an end; pure monochloroacetone boiling at $118\text{--}120^\circ$ can then be isolated from the product by fractional distillation. When molecular proportions of acetone and marble are used, and chlorine is passed until the latter is almost completely dissolved, about 90 per cent. of a mixture of mono- and di-chloroacetone boiling at $118\text{--}120^\circ$, and about 10 per cent. of symmetrical dichloroacetone melting at 44° , are obtained.

When monochloroacetone is treated with chlorine at 100° in sunlight as long as the gas is absorbed, the principal product is pentachloroacetone boiling at about $190\text{--}195^\circ$. F. S. K.

Action of Nitric acid on Acetone. By R. BEHREND and J. SCHMITZ (*Ber.*, 26, 626—628).—A yellow, very unstable oil which seems to consist for the most part of *hydroxyisonitrosoacetone nitrite*, $\text{COMe}\cdot\text{C}(\text{NOH})\cdot\text{O}\cdot\text{NO}$, is formed, together with carbonic oxide, carbonic anhydride, nitrous oxide, nitrogen, ammonia, acetic acid, and oxalic acid, when acetone is carefully treated with nitric acid of sp. gr. 1.37, to which a little red fuming acid has been added. It is decomposed by concentrated hydrochloric acid, with evolution of gas, yielding *chlorisonitrosoacetone*, $\text{COMe}\cdot\text{CCl}\cdot\text{NOH}$; this compound melts at $104.5\text{--}105.5^\circ$, and combines with hydroxylamine to form chloromethylglyoxime, which decomposes at about 175° ; chlorisonitrosoacetone is decomposed by boiling dilute sulphuric acid, the products being acetic, formic, and hydrochloric acids and hydroxylamine.

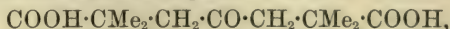
The *oxime*, $\text{C}_3\text{H}_5\text{N}_3\text{O}_4$, is obtained when an aqueous solution of the yellow, unstable oil is treated with hydroxylamine hydrochloride. When the crude crystalline product is dissolved in ether, and the solution is mixed with light petroleum, a small quantity of an oxime, which decomposes at about 148° , is precipitated; on evaporating the solution large, transparent crystals, which contain ether and effloresce on exposure to the air, are deposited; these crystals, when free from ether, decompose at $97\text{--}98^\circ$, but sinter at about 80° . The oxime gives Liebermann's reaction, is very unstable, and decomposes with

evolution of ruddy fumes, even when kept in closed vessels or when warmed with benzene or chloroform; on treatment with concentrated hydrochloric acid, it yields chlorisonitrosoacetone and a small quantity of chloromethylglyoxime, with evolution of gas. On adding sodium carbonate to an aqueous solution of the oxime, carbonic anhydride is liberated, the solution turns yellow, and a sparingly soluble, crystalline powder is precipitated, sodium nitrite remaining in solution; the crystalline precipitate separates from hot alcohol in small needles, decomposes at about 191° , dissolves in alkalis yielding colourless solutions, and has the composition $C_3H_4N_2O_2$.

The *hydrazone*, $N_2HPh \cdot CMe \cdot C(NO \cdot H) \cdot O \cdot NO$, is produced, together with a small quantity of a hydrazone which decomposes at about 177° , when the yellow, unstable oil is treated with phenylhydrazine hydrochloride; it crystallises from a mixture of ether and petroleum in long, transparent, amber-yellow prisms or plates, which contain ether, effloresce on exposure to the air, and decompose at 125° .

F. S. K.

Formation of Phoronic acid from Phorone. By R. ANSCHÜTZ (*Ber.*, 26, 827—828).—Phorone, melting at 28° , prepared from acetone and hydrochloric acid, is treated with gaseous hydrogen chloride until it has taken up 2 molecular proportions of the latter, the product is boiled in alcoholic solution with potassium cyanide, and the phoronitrile which separates on warming with fuming hydrochloric acid is hydrolysed, and yields phoronic acid melting at 184° ; hence the formulæ previously assigned to phorone, $CMe_2 \cdot CH \cdot CO \cdot CH \cdot CMe_2$, and to phoronic acid,



are confirmed.

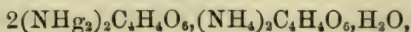
C. F. B.

New Mercurammonium Salts. By E. BALESTRA (*Gazzetta*, 22, ii, 563—569).—*Mercurammonium acetate*, $NHg_2 \cdot OAc$, is obtained as a white powder on digesting yellow mercuric oxide with ammonium acetate solution; it becomes slightly yellow on exposure to air, and is turned brown by light. It dissolves in hydrochloric acid or ammonium acetate, but is insoluble in water.

Mercurammonium ammonium acetate, $NHg_2 \cdot AcO, 3NH_4 \cdot OAc, H_2O$, is obtained in deliquescent, colourless prisms by the slow evaporation of mercuric acetate solution rendered slightly alkaline by ammonia; the same salt is formed on saturating a concentrated solution of ammonium acetate with yellow mercuric oxide. It is soluble in a little water without decomposition, but mercurammonium acetate separates on adding much water.

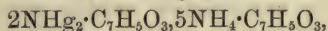
Mercurammonium tartrate, $(NHg_2)_2C_4H_4O_6 \cdot 2\frac{1}{2}H_2O$, is prepared by spontaneous evaporation of a solution of mercuric tartrate in ammonia or of yellow mercuric oxide in ammoniacal ammonium tartrate solution. It forms colourless, prismatic masses, is very sensitive to light, and is soluble in hydrochloric acid, potassium iodide, sodium thiosulphate, and ammonium acetate or tartrate solutions, but insoluble in water.

Mercurammonium ammonium tartrate,



separates as a white, amorphous powder when yellow mercuric oxide is dissolved in ammonium tartrate; it resembles the preceding salt in chemical properties.

Mercurammonium ammonium salicylate,



separates in opaque prisms from a solution of yellow mercuric oxide in ammonium salicylate. It dissolves in ammonium acetate, tartrate, or bromide, hydrochloric acid, or potassium iodide solutions, but is decomposed by water.

W. J. P.

Mixed Anhydrides of Hypochlorous and analogous acids.

By T. SELIVANOFF (*Ber.*, 26, 423—426; compare this vol., i, 192).—Bromylacetamide, NHAcBr ("acetobromamide" of Hofmann), is shown to be a substituted amide of hypobromous acid, for when it is distilled with water at a low pressure the distillate contains much hypobromous acid and but little bromine, and acetamide is regenerated. Moreover, from a solution of potassium iodide acidified with acetic acid, 1 mol. of bromylacetamide liberates 2 atoms of iodine, and thus reacts like 1 mol. of hypobromous acid. Dibromylacetamide, NACBr_2 , in a similar way displaces 4 atoms of iodine, and is thus to be regarded as a substituted imide of hypobromous acid (2 mols.). With amines and acid amides, bromylacetamide behaves like the analogous chlorine compound. With dipropylamine, it yields acetamide and bromyldipropylamide, NPr_2Br , the latter as an oil. With succinimide, it yields bromylsuccinimide, $\text{C}_2\text{H}_4\cdot\text{C}_2\text{O}_2\cdot\text{NBr}$, melting at $161\text{--}162^\circ$; this substance can also be synthesised from succinimide and hypobromous acid, or bromine and an alkali, and it is decomposed by water into hypobromous acid and succinimide. With ethylic imido-carbonate, it yields the bromylimidocarbonate, $\text{NBr}\cdot\text{C}(\text{OEt})_2$, 1 mol. of which also liberates 2 atoms of iodine. With amylamine, it yields dibromylamylamide, NAmBr_2 , as a reddish-brown, unstable oil, with a strong, unpleasant odour; in the presence of water it reacts like 2 mols. of hypobromous acid. Besides the above-mentioned compounds, bromyldimethylamide, NMe_2Br , dibromylethylamide, NEtBr_2 , and bromyldiisobutylamide, NBu^iBr_2 , were prepared. These substances react like those already described; they are less stable than the corresponding chlorine compounds, and are more easily hydrolysed. Some of the secondary amine derivatives are explosive.

C. F. B.

Synthesis with the aid of Ethylic Cyanacetate and Ethylic Cyanosuccinate. By L. BARTHE (*Ann. Chim. Phys.*, [6], 27, 239—288).—The experiments which have been previously recorded in various short papers (*Abstr.*, 1889, 588, 708; 1891, 42, 43, 1017) are now communicated in a systematic form, but without any new facts of importance being given.

F. S. K.

Oxidation Products of Behenolic acid. By O. v. GROSSMANN (*Ber.*, 26, 639—649).—Behenolic acid is prepared by the bromination of erucic acid and treatment of the product with potash at 180° ; the yield is about 75 per cent. of the theoretical.

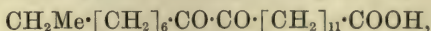
On oxidising behenolic acid with concentrated fuming (red) nitric acid.

acid, carbonic anhydride is evolved; the oily portion is separated, and steam distilled, when the distillate consists of pelargonic acid and ethyl pelargonate, together with a small quantity of an acid which gives a yellow, crystalline barium salt, and is probably nitroso-pelargonic acid. The non-volatile residue contains dioxybehenolic acid (m. p. 93.5°), and arachic acid (m. p. 73.5°), which are separated by means of light petroleum, in which the former is insoluble.

The aqueous nitric acid solution contains brassylic acid, which, contrary to the statements of Haussknecht, melts at 112° , has the formula $C_{13}H_{24}O_2$, and is formed, together with pelargonic acid, by the action of fuming nitric acid on dioxybehenolic acid. The barium salt crystallises with 2 mols. H_2O ; the calcium and copper salts with 1 mol. H_2O ; whilst the silver salt is anhydrous.

Behenolic acid, on fusion with potash, yields arachic acid and acetic acid.

Two distinct reactions appear to take place during the oxidation of behenolic acid, $CH_2Me \cdot [CH_2]_{11} \cdot C:C \cdot COOH$; on the one hand, it yields carbonic anhydride and arachic acid, $CH_2Me \cdot [CH_2]_{11} \cdot COOH$, whilst a portion of it is converted into dioxybehenolic acid,



which is then resolved into pelargonic acid, $CH_2Me \cdot [CH_2]_6 \cdot COOH$, and brassylic acid, $COOH \cdot [CH_2]_{11} \cdot COOH$. The author does not consider that "behenolic acid" is an isomeric mixture, but that the nitric acid causes an intramolecular rearrangement of the hydrogen atoms.

J. B. T.

Heintz's Glycollide. By R. ANSCHÜTZ (*Ber.*, 26, 560—562; compare this vol., i, 165, and Bischoff and Walden, this vol., i, 250).—The author shows, by reference to Heintz's paper (*Pogg. Ann.*, 109, 484), that the latter had in his hands the diglycollide corresponding to lactide, having obtained it as a crystalline substance by distilling glycollic acid in a current of carbonic anhydride. He appears not to have further investigated this substance after finding that glycollic acid, on heating at 240° , gives the glycollide melting at 220° , which he supposed to correspond with lactide. The author has repeated Heintz's experiment, carrying out the distillation under diminished pressure, and finds that the substance thus obtained has the composition $C_2H_2O_2$, and like dilactide, but unlike the glycollide already known, is soluble in chloroform, after crystallising from which it melts at $82-83^{\circ}$. When again distilled under diminished pressure, it passes into polyglycollide.

H. G. C.

Ethylic Carbacetoacetate. By P. GENVRESSE (*Bull. Soc. Chim.* [3], 7, 586—587).—A rejoinder to Hantzsch (*Abstr.*, 1892, 819).—The author states that he has experimentally proved the non-identity of the so-called ethylic carbacetoacetate and ethylic isodehydracetate. In repeating Hantzsch's experiments, he has not obtained the homomesaconic acid described by the latter, but two entirely different acids, in accordance with Anschütz's results (*Abstr.*, 1892, 172).

A. R. L.

Action of Iodic acid on Malonic acid. By A. ANGELI (*Ber.*, 26, 595—597).—*Triiodacetic acid*, $\text{Cl}_3\cdot\text{COOH}$, is obtained when malonic acid is treated with a hot aqueous solution of iodic acid, and the mixture boiled until a rapid evolution of carbonic anhydride commences; if, after cooling quickly, the solution be kept for 2 or 3 days, the new acid is deposited in lustrous, yellow crystals, which turn brown at 100° , and melt at 150° with decomposition; it is decomposed by warm acetic acid into iodoform and carbonic anhydride.

Diiodacetic acid is also formed when malonic acid is treated with iodic acid, and can be obtained as the principal product by boiling the solution until the evolution of carbonic anhydride is at an end, filtering from the precipitated triiodo-derivative, and again boiling for some time; on cooling, the acid is deposited in pale yellow needles melting at 110° . F. S. K.

Ethereal Salts of Pyrotartaric acid. By R. BRAUNSCHWEIG (*J. pr. Chem.* [2], 47, 274—300).—The etherification of pyrotartaric acid with methyl or ethyl alcohol gives rise to mixtures of normal and acid ethereal salts, in which the former predominate. It is not settled whether the acid salts belong to the ortho-series,



or the allo-series, $\text{COOH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{COOR}$, or to both; they are also obtainable by heating pyrotartaric anhydride with the corresponding alcohol, as in the case of the ortho-salts of camphoric acid. By treating an alcoholic solution of pyrotartaric anhydride with sodium or sodium alkylxide, the sodium ethereal salt is obtained, and the acid ethereal salt obtained by decomposing this is found to be identical with that obtained directly, as indicated above. The acid salts can also be prepared by partial hydrolysis of the normal salts, but whether the products belong to the allo- or ortho-series is not settled. The mixed salts are difficult to obtain, and isomerides have not yet been isolated.

Dimethylic pyrotartrate may be prepared by saturating a solution of pyrotartaric acid in methyl alcohol with dry hydrogen chloride, precipitating the oily product by a solution of salt, dissolving it in light petroleum, and extracting any methylic hydrogen pyrotartrate from this solution by a weak alkali. It is a colourless liquid, has a peculiar odour, boils at 197° (759 mm.), and dissolves in water, from which it is separated by salt. Its optical properties are detailed.

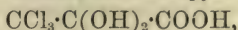
Orthomethylic pyrotartrate is prepared by heating pyrotartaric anhydride (b. p. $240\text{--}240.5^\circ$, obtained by heating pyrotartaric acid in a stream of air as long as water is expelled) with methyl alcohol in a reflux apparatus. It is a colourless, strongly acid liquid, which boils at $153\text{--}153.5^\circ$ (20 mm.); it dissolves in water, but may be salted out again unless it has been left long enough to undergo hydrolysis into methyl alcohol and pyrotartaric acid. The *sodium derivative* is obtained as a gelatinous precipitate by adding sodium methoxide to a solution of pyrotartaric anhydride in glacial acetic acid.

Orthoethylic pyrotartrate is similarly prepared; it is a colourless, odourless oil, boils at $160\text{--}161^\circ$ (22 mm.), and dissolves in water, from which it may be salted out. The *sodium derivative* was prepared.

Experiments made with the object of obtaining mixed alkyl pyrotrates are detailed. The *ethylic methylic* salt, prepared by the action of sodium on a mixture of the orthoethylic salt and methylic iodide, was found to be a colourless, refractive liquid, which distilled for the most part at 198—199° (754.1 mm.); its optical properties are given.

A. G. B.

Trichloropyruvic acid. By O. BÜCHNER (*Ber.*, 26, 656—658).—Chlorofumaric acid is dissolved in 6 parts of water, and the solution repeatedly saturated with chlorine until the colour is permanent; the operation requires about two weeks; after extraction with ether and crystallisation from chloroform, trichloropyruvic acid,



is obtained, and is identical with "isotrichloroglyceric acid" prepared by Schreder from gallic acid and salicylic acid by the action of hydrochloric acid and potassium chlorate, and by Claisen and Antweiler from trichloroacetyl cyanide. On treatment with alkalis, hydroxylamine, or phenylhydrazine at the ordinary temperature, it is resolved into oxalic acid and chloroform; by reduction in acid solution, hydroxypropionic acid is formed. *Ethylic trichloropyruvate* boils at 110° under a pressure of 21 mm.; it forms colourless crystals containing 1 mol. H_2O , and melts at 34.5°.

J. B. T.

Action of Hydrogen Sulphide on Pyruvic acid. By J. M. LOVÉN (*J. pr. Chem.* [2], 47, 173—182).—The author has already dealt with this subject (*Abstr.*, 1884, 1298); he further discusses the trithiodilactylic acid, $\text{C}_6\text{H}_{10}\text{S}_3\text{O}_4$, obtained by saturating a 50 per cent. aqueous solution of pyruvic acid with hydrogen sulphide, and adding fuming hydrochloric acid until the solution becomes turbid. The oily liquid which now separates soon crystallises, and may be recrystallised from chloroform. It forms lustrous laminae, melts at 95°, and dissolves in hot water, from which it separates out on cooling in the oily form, but afterwards solidifies; dilute acids dissolve it but little. It has an acid reaction, and decomposes carbonates. Alkalis remove sulphur from it, even in the cold. Lead acetate gives a white and copper acetate a greenish precipitate, with the acid, but both precipitates soon turn black from formation of sulphide. By elimination of sulphur, it yields dithiodilactylic acid (*loc. cit.*); by reduction with hydrogen it yields hydrogen sulphide and thiolactic acid; by oxidation, it yields barium α -sulphopropionate. From these reactions, the author deduces that the formula $\text{S}(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{COOH})_2$ correctly represents the constitution of the acid.

A. G. B.

Solubility of Cream of Tartar in Dilute Alcohol. By W. H. WENGER (*Amer. Chem. J.*, 14, 624—625).—The figures in the lower line give the number of grams of cream of tartar which dissolve at 25° in 1000 c.c. of aqueous alcohol of the percentage strength given by the corresponding figure in the upper line.

90.	80	70.	60.	50.	40.	30.	20.	10.	Water.
0.15	0.19	0.30	0.41	0.79	1.32	1.96	3.01	4.51	5.76

C. F. B.

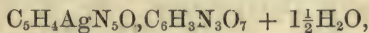
Constitution of Leucine. By E. SCHULZE and A. LIKIERNIK (*Zeit. physiol. Chem.*, **17**, 513—535).—A full account is given of experiments previously published (*Abstr.*, 1891, 681). In addition, it is found that leucine prepared from various sources, fibrin, elastic tissue, &c., has the same properties as those already described in the leucine obtained from conglutin. W. D. H.

Nuclein Bases. By C. WULFF (*Zeit. physiol. Chem.*, **17**, 468—510).—The following method is recommended for the separation of guanine from guano. It is boiled for four hours with dilute sulphuric acid, cooled, and filtered; the filtrate is made alkaline with sodium hydroxide and again filtered. To the filtrate, ammoniacal silver solution is added, to precipitate the guanine and uric acid; this precipitate is washed with cold water and hot water, and then treated with hot dilute hydrochloric acid, the silver chloride filtered off, and the filtrate decolorised with animal charcoal; the guanine is then precipitated therefrom by ammonia; a small quantity of urea in hot nitric acid is added, and the mixture is set aside to crystallise. The guanine nitrate, now free from uric acid, is dissolved in dilute sodium hydroxide and the guanine precipitated by ammonium chloride. This last procedure gets rid of traces of xanthine.

Guanine exists in guano partly as a calcium compound and partly in substances like nuclein. From these it is liberated by the preliminary treatment with hot sulphuric acid.

The decomposition of guanine by hydrochloric acid is represented by the equation $C_5H_5N_5O + 7H_2O = 4NH_3 + C_2H_5NO_2 + 2CO_2 + CH_2O_2$.

The compounds of guanine investigated were the *dichromate*, $C_5H_5N_5O, H_2Cr_2O_7$, orange-coloured, four-sided prisms, giving off water when heated at 100° ; the *picrate*, $C_5H_5N_5O, C_6H_3N_3O_7 + H_2O$, yellow needles, losing water of crystallisation at 110° and decomposing at 190° ; the *ferricyanide*, $(C_5H_5N_5O)_4, H_3Fe(CN)_6 + 8H_2O$, brown, six-sided prisms, losing water of crystallisation at 120 — 130° ; the *nitroferri-cyanide*, $(C_5H_5N_5O)_2, H_2(CN)_5NOFe + 1\frac{1}{2}H_2O$, four-sided prisms; the *metaphosphate*, $C_5H_5N_5O, HPO_3 + xH_2O$, readily soluble in water and dilute acids, but sparingly in ammonia; these solubilities go against Liebermann's hypothesis, that nuclein is proteid metaphosphate; adenine forms an analogous compound. The *silver picrate*,



is sparingly soluble in hot, insoluble in cold water; the *bismuthiodide* has the formula $C_5H_5N_5O, HI, 2BiI_3 + 2H_2O$.

Acetylguanine, $C_5H_4N_5OAc$, is crystalline and sparingly soluble in water, alcohol, and ether, it may be heated to 260° without change; *propionylguanine*, $C_5H_4N_5O \cdot COEt$, is crystalline and may be heated to 260° without change; *benzoylguanine*, $C_5H_4N_5O \cdot COC_6H_5$, is crystalline, obtainable with difficulty in small quantities; and a crystalline ethylguanine, $C_5H_4EtN_5O$, may be heated to 280° without change. Attempts to obtain a dimethyl derivative failed.

The formation of the picrate is recommended for estimation of

guanine. Full details with test experiments are given. Metaphosphoric acid may be used for the separation of guanine from hypoxanthine and adenine, but there are difficulties yet to be overcome.

An appendix to the paper gives details concerning hypoxanthine picrate, adenine metaphosphate, and adenine aurochloride.

W. D. H.

Oxidation Products of some Substances containing the Group of Atoms $C_2N_2O_2$. By A. ANGELI (*Ber.*, 26, 593—595).—The peroxides of certain fatty oximes containing aromatic radicles,

that is to say, compounds of the general formula $\begin{array}{c} CMe-CR \\ || \quad || \\ N \cdot O \cdot O \cdot N \end{array}$, such as those derived from isosafrole, isoapiole, &c., contain a very stable closed chain, and, on treatment with potassium permanganate, are sometimes converted into acids simply by the oxidation of the aromatic radicle.

An acid of the constitution $\begin{array}{c} N: CMe \\ | \\ O \cdot O \cdot N \end{array} > C \cdot COOH$ is formed when diisonitrosoisosafrole peroxide, $\begin{array}{c} N: CMe \\ | \\ O \cdot O \cdot N \end{array} > C \cdot C_6H_3 < \begin{array}{c} O \\ | \end{array} > CH_2$, is oxidised with potassium permanganate in alkaline solution; it crystallises in colourless plates or needles, and melts at 92° . That the constitution of this compound is expressed by the formula given above, is shown by the fact that it can also be obtained by oxidising $\alpha\beta$ -diisonitrosobutyric acid with ice-cold nitric acid of sp. gr. 1.45.

It would seem that the direct combination of an unsaturated compound with nitrous acid is greatly facilitated when the former contains two double linkings in close proximity, even when one is present in a closed chain; derivatives of propenylbenzene, for example, are readily converted into crystalline compounds of the general formula $R \cdot C_3H_5 \cdot N_2O_3$ and $R \cdot C_3H_3 \cdot N_2O_2$, whereas the corresponding allyl derivatives are practically unchanged under the same conditions. Again, crotonic acid does not yield an additive product with nitrous acid, whereas sorbic acid, which, according to Fittig, has the constitution $CHMe:CH:CH:CH \cdot COOH$, is readily converted into a nitrosite.

F. S. K.

Nitrogen Halogen Compounds. By F. LENGFELD and J. STIEGLITZ (*Amer. Chem. J.*, 15, 215—222).—Bromosuccinimide,

$\begin{array}{c} CH_2 \cdot CO \\ | \\ CH_2 \cdot CO \end{array} > NBr$, is obtained by the action of bromine (32 grams) on succinimide (20 grams) dissolved in ice-cold aqueous soda (8 grams to 50 c.c.). It crystallises from hot benzene in colourless, tetragonal prisms, and melts at 172.5° when slowly heated, but at 177.5 — 178.5° when rapidly heated. With acids, bromine is liberated, and succinimide regenerated, whilst with ammonia, nitrogen is evolved. It is slowly decomposed by water, but is quite stable when dry. When boiled with sodium methoxide (1 mol.) in dilute methyl alcohol solution, it forms two compounds, one of which, methoxysuccinamic

acid, $\text{OMe}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, a colourless, crystalline substance melting at $77-77.5^\circ$, and formed only in small quantity, is sparingly soluble in ether, and the other, the *methylic salt* of this acid, a colourless, crystalline substance melting at 33.5° and boiling at $145.5-146.5^\circ$ under 20 mm. pressure, is easily soluble. When the sodium methoxide solution is concentrated, a small quantity of methylic methoxysuccinamate is formed, together with some succinimide, but the greater part of the product consists of a colourless, crystalline substance, $\text{C}_{10}\text{H}_{16}\text{O}_6\text{N}_2$, which is hydrolysed by cold, concentrated hydrochloric acid yielding succinic acid and a neutral, colourless, crystalline substance, $\text{C}_4\text{H}_6\text{O}_5\text{N}_2$, melting with decomposition at 272° . The latter may also be obtained from the former by boiling it with a methyl alcohol solution of sodium methoxide (1 mol.). JN. W.

Furfuryl Alcohol and its Derivatives. By L. V. WISELL and B. TOLLENS (*Annalen*, **272**, 291—306).—Furfuryl alcohol, prepared by Schiff's method (*Abstr.*, 1891, 676) and purified by distillation with steam, boils at $168-170^\circ$, and is soluble in water; its sp. gr. is 1.1354 at $20^\circ/20^\circ$. Like pyrroline, it is very sensitive to mineral acids; the pure alcohol does not redden aniline acetate paper.

Furfuryl methyl ether, $\text{C}_5\text{H}_6\text{O}\cdot\text{OMe}$, obtained by treating furfuryl alcohol with potassium hydroxide and methylic iodide, is a colourless, pleasant smelling liquid of sp. gr. 1.0315 at $20^\circ/20^\circ$, and boils at $134-136^\circ$.

Furfuryl ethyl ether, $\text{C}_5\text{H}_6\text{O}\cdot\text{OEt}$, is a mobile oil of sp. gr. 0.9884 at $20^\circ/20^\circ$; it boils at $148-150^\circ$. The *propyl ether*, $\text{C}_5\text{H}_6\text{O}\cdot\text{OPr}$, boils at $164-168^\circ$; its sp. gr. is 0.9722 at $20^\circ/20^\circ$. The *amyl ether*, $\text{C}_5\text{H}_6\text{O}\cdot\text{O}\cdot\text{C}_5\text{H}_{11}$, boils at $196-198^\circ$, and is specifically lighter than water.

Furfurylic benzoate, $\text{C}_5\text{H}_6\text{O}\cdot\text{OBz}$, prepared by shaking the alcohol with soda and benzoic chloride, seems to boil at $275-285^\circ$; its sp. gr. is about 1.1766 at $20^\circ/20^\circ$. The corresponding *acetate*, $\text{C}_5\text{H}_6\text{O}\cdot\text{OAc}$, boils at $175-177^\circ$; its sp. gr. is 1.1175 at $20^\circ/20^\circ$. F. S. K.

Methylfurfuraldehyde and Methylpyromucic acid. By H. B. HILL and W. L. JENNINGS (*Amer. Chem. J.*, **15**, 159—185).—Wood was subjected to dry distillation at a comparatively low temperature, and a considerable amount of furfuraldehyde was formed, together with substances of higher boiling point ($175-250^\circ$), which were ultimately resolved by fractionation with a Hempel bead column into two liquids, boiling at $184-186^\circ$ and $200-220^\circ$ respectively. The first, nearly colourless, and forming the larger part of the product, showed the general properties of an aldehyde, and on purification by means of the hydrogen sodium sulphite compound, proved to be methylfurfuraldehyde, boiling at $186-187^\circ$ (corr.) under a pressure of 760 mm., and having a sp. gr. of 1.1087 at $18^\circ/18^\circ$. It smells like its lower homologue, forms a liquid hydrazone with phenylhydrazine, gives colour tests with diazobenzenesulphonic acid, with resorcinol and hydrochloric acid (orange-red), and with pyrogallol (carmines), but apparently does not restore the colour to rosaniline decolorised by sulphurous acid. With aqueous ammonia, like aromatic aldehydes, it

yields *methylfurfuramide*, $C_{18}H_{18}N_2O_3$, a substance crystallising in slender, radiating needles, and melting at 86—87°. Both methylfurfuraldehyde and its lower homologue are converted quantitatively into the corresponding acids by oxidation with silver oxide in boiling aqueous solution.

Methylpyromucic acid, $C_4OH_2Me \cdot COOH$, crystallises in hexagonal prisms or plates, melts at 108—109°, and sublimes readily at low temperatures. The *barium salt* (anhydrous), *calcium salt*, with $2H_2O$, *silver salt* (anhydrous), *sodium salt* (anhydrous) and *potassium salt* (anhydrous) are described. The *ethylic salt* boils at 213—214° under a pressure of 766 mm., and does not crystallise. It is converted by ammonia into *methylpyromucamide*, $C_4OH_2Me \cdot CONH_2$, which forms long, colourless prisms, and melts at 131°. Methylpyromucic acid is oxidised by moist bromine (2 mols.), with elimination of carbonic anhydride, yielding β -acetacrylic acid, $CHAc:CH \cdot COOH$, melting at 123—124°, but by the addition of bromine, it is converted into $\alpha\beta$ -dibromolevulinic acid, melting at 107—108°, which yields a phenylhydrazone, $NHPh \cdot N:CMc:CH:CH \cdot COOH$, melting at 156—157°. The methyl group of methylpyromucic acid is, therefore, in the δ -position. Methylpyromucic acid is converted by fuming sulphuric acid into a *sulphomethylpyromucic acid*, in which the sulphonic group is probably in the β -position. Dry bromine acting in the cold (in glacial acetic acid solution) effects nuclear substitution, as in aromatic compounds, a *bromomethylpyromucic acid*, $C_4OHBrMe \cdot COOH$, being formed, which crystallises in colourless, branching needles and melts at 150—151°. The *barium salt* with $4H_2O$, *calcium salt* with $3H_2O$, *silver salt* (anhydrous), and *potassium salt* (anhydrous) are described. Moist bromine (bromine vapour, 2 mols., passed into aqueous solution) or dilute nitric acid oxidises and hydrolyses the bromo-acid into a bromoacetylacrylic acid melting at 61°, the exact constitution of which has not yet been determined. A small quantity of a crystalline substance melting at 90—91° and containing a large amount of bromine is simultaneously formed by the action of the latter. Bromine acting on methylpyromucic acid in boiling carbon bisulphide or chloroform solution effects substitution in the lateral chain, again as with aromatic compounds, *w-bromomethylpyromucic acid*, $CH_2Br \cdot C_4OH_2 \cdot COOH$, being formed. This crystallises in small, clustered, oblique plates, and melts at 147—148°. It is hydrolysed by hot water into hydrogen bromide and *w-hydroxymethylpyromucic acid*, $OH \cdot CH_2 \cdot C_4OH_2 \cdot COOH$, melting at 162—163°, and thus resembles the aromatic lateral chain substitution products. By brominating the nucleal bromomethylpyromucic acid in boiling chloroform, lateral chain substitution is effected, and *w β -dibromomethylpyromucic acid* is formed. This crystallises in small, oblique tables, and melts with decomposition at 175°. It is hydrolysed by water into *w-hydroxy- β -bromomethylpyromucic acid*, which crystallises in oblique prisms, and melts at 153—154°. The *barium salt* is mentioned. Like aromatic compounds, methylpyromucic acid forms unstable additive products. The acid in chloroform solution, for instance, when cooled by a freezing mixture, takes up bromine (4 atoms) to form the tetrabromide of methylpyromucic acid,

$C_4OH_2MeBr_4 \cdot COOH$, which crystallises in flat needles, and melts with decomposition at about 95° .

The fraction boiling at $200-220^\circ$ was extracted with alkali, and the acidified alkaline extract distilled with steam; an oil was obtained which boiled at $200-205^\circ$, and proved to be guaiacol (orthomethoxyphenol), since it was converted by bromine into tribromoguaiacol (m. p. $115-116^\circ$) and the latter by hydrolysis into catechol (m. p. $103-104^\circ$; b. p. $240-242^\circ$). J. N. W.

Derivatives of Pyromucamide. By C. E. SAUNDERS (*Amer. Chem. J.*, **15**, 130—137).— $\beta\delta$ -Dibromofurfuronitrile is prepared by dissolving $\beta\delta$ -dibromopyromucamide in bromine (6 atomic proportions) and treating the solution with a cold 5 per cent. solution of sodium hydroxide, when it rises to the surface. It was also obtained by dehydrating $\beta\delta$ -dibromopyromucamide by means of phosphorus pentachloride. It crystallises from superheated alcohol in colourless laminae, has a characteristic odour, melts at 88° (uncorr.), boils at 225° (uncorr.), and can be sublimed; it dissolves in ether and hot alcohol, but hardly at all in water. When acted on by concentrated hydrochloric acid, it yields the original amide and $\beta\delta$ -dibromopyromucic acid.

Pyromucamide tetrabromide is obtained by the direct action of bromine on pyromucamide below 0° . It forms colourless, lustrous crystals, melts about 121° , and dissolves to some extent in ethylic acetate and acetone, but is almost insoluble in most other organic solvents and quite insoluble in water. It is decomposed by boiling with water, glacial acetic acid, or alcohol. Alkalis decompose it with the formation of $\beta\gamma$ -dibromopyromucic acid.

When pyromucamide is dissolved in bromine water and the solution is made alkaline, a dark blue (or purple) colour is produced. If aniline be the base employed, a reddish precipitate is produced, which melts with decomposition at 78° . When phenylhydrazine is used, a brilliant, red precipitate is obtained; this can be crystallised from an alcoholic solution saturated at 50° ; its composition is $C_{11}H_{11}N_3O_2$, corresponding with a compound of 1 mol. of phenylhydrazine with 1 mol. of pyromucamide, less 2 atoms of hydrogen. It is being further investigated. A. G. B.

Chlorosulphopyromucic acids. By H. B. HILL and W. S. HENDRIXSON (*Amer. Chem. J.*, **15**, 145—158).— β -Chloropyromucic acid, prepared by the action of sodium amalgam on the $\beta\gamma$ -dichloro-acid, is converted by fuming sulphuric acid into β -chloro- δ -sulphopyromucic acid, $SO_3H \cdot C_4OHCl \cdot COOH$, which crystallises in hemispherical masses of indistinct, radiating needles, and is deliquescent. The *barium salt* ($+ H_2O$), *lead salt* ($+ 4H_2O$), and *potassium salt* ($+ H_2O$) are described. On attempting to eliminate the chlorine by means of sodium amalgam in alkaline solution, the sulphonic group is itself eliminated, and the chloro-acid re-formed. This behaviour is characteristic of the δ -sulphopyromucic acids. The sulphonic group is also eliminated by oxidation with bromine, chlorofumaric acid apparently

being formed. Fuming nitric acid converts the chlorosulphonic acid into the corresponding β -chloro- δ -nitropyromucic acid with H_2O .

$\beta\gamma$ -Dichloropyromucic acid is converted by fuming sulphuric acid into $\beta\gamma$ -dichloro- δ -sulphopyromucic acid, $\text{SO}_3\text{H}\cdot\text{C}_4\text{OCl}_2\cdot\text{COOH}$, which crystallises in radiating needles and is deliquescent. The barium salt with $5\text{H}_2\text{O}$, lead salt with $3\text{H}_2\text{O}$, and potassium salt with H_2O are described. The sulphonic group is eliminated by oxidation with bromine, dichloromaleic acid being formed.

δ -Chloropyromucic acid is converted by fuming sulphuric acid into β -sulpho- δ -chloropyromucic acid, which crystallises in dendritic needles. The barium salt with $5\text{H}_2\text{O}$, acid barium salt with $4\text{H}_2\text{O}$, calcium salt with $2\text{H}_2\text{O}$, lead salt with H_2O , and potassium salt (anhydrous) are described. The sulphonic acid yields β -sulphopyromucic acid on reduction with zinc dust in ammoniacal solution. On oxidation with bromine, it yields either sulphofumaric acid or $\alpha\alpha$ -chlorobromofurfuran- β -sulphonic acid, as the bromine is in excess or limited (1 mol.). The latter acid forms a waxy, deliquescent mass when its aqueous solution is evaporated. The barium salt with H_2O , calcium salt with $2\text{H}_2\text{O}$, lead salt with H_2O , and potassium salt (anhydrous) are described.

JN. W.

Reactions of Dimolecular Nitriles. By P. S. BURNS (*J. pr. Chem.* [2], 47, 105—134).—Throughout this paper the author substitutes the terms dipropionitrile and diacetonitrile for imidopropionylethyl cyanide and imidoacetylmethyl cyanide respectively (Abstr., 1889, 114). The compounds of benzoyl with dipropionitrile have been already described (Abstr., 1891, 888; 1892, 450). The compound $\text{NBz}:\text{CMe}\cdot\text{CHBz}\cdot\text{CN}$ (m. p. 158°) is now called dibenzoyldiacetonitrile; it and its reactions have also been described (Abstr., 1892, 450).

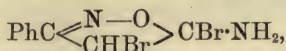
Benzoyldiacetonitrile, $\text{NBz}:\text{CMe}\cdot\text{CH}_2\cdot\text{CN}$, is prepared by mixing ethyl-ic benzoate, sodium ethoxide, and diacetonitrile in well cooled ether and completing the reaction on the water bath; the sodium compound separates and is decomposed by water. It crystallises in long, white needles, melts at 82° , and is soluble in most solvents except dilute acids, alkalis, and water. It is isomeric with the imido-derivative (m. p. 148°) obtained by the action of ammonia on α -cyanobenzoyl-acetone (*loc. cit.*); by hydrolysis, it is decomposed into cyanacetone, ammonia, and benzoic acid.

Benzoylbenzacetoneitrile, $\text{N}\begin{smallmatrix} \text{CPh}(\text{OH}) \\ \text{CPh} \end{smallmatrix} > \text{CH}\cdot\text{CN}$, is the product of the action of benzoic chloride on benzacetodinitrile; it crystallises in small, silky, yellow needles, melts at 250° , and dissolves in benzene, carbon bisulphide, and acetone, but not in ether, alcohol, acids, or alkalis. It is remarkably stable and can be dissolved in strong sulphuric acid without change; it does not form salts.

Cyanacetoxime, $\text{NOH}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CN}$, is obtained by the action of hydroxylamine hydrochloride on diacetonitrile in concentrated aqueous solution; it crystallises in long needles, melts at 96° , and is soluble in ether, alcohol, hot benzene, and alkalis; its acetyl derivative crystallises in small prisms, and melts at 169° . Hot hydrochloric acid converts it into cyanacetone and hydroxylamine hydrochloride. When heated with water, it undergoes isomeric change, becoming methyl-

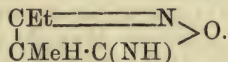
isoxazonimide, $\text{N} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CMe} \cdot \text{CH}_2 \end{smallmatrix} \text{C:NH}$, which forms feathery crystals, melts at 84° , and is easily soluble in water, alcohol, ether, and benzene; its hydrochloride was prepared. Hot hydrochloric acid decomposes it with formation of ammonium chloride.

Phenylisoxazonimide, $\text{C}_9\text{H}_8\text{N}_2\text{O}$, is produced when hydroxylamine acts on benzacetodinitrile; it has been already obtained (Obrégia, Abstr., 1892, 324) by the action of hydroxylamine on cyanacetophenone in alkaline solution. Hydrochloric acid converts it into phenylisoxazolone (Abstr., 1891, 468). The *hydrochloride* and *acetyl derivative* (m. p. 164°) of the imide were prepared. In ethereal solution it absorbs 2 atoms of bromine, forming the compound



which is white, crystalline, and melts with decomposition at $128-130^\circ$; water converts it into the monobromo-derivative, $\text{PhC} \begin{smallmatrix} \text{N}-\text{O} \\ \diagup \quad \diagdown \\ \text{CHBr} \end{smallmatrix} \text{CO}$, which crystallises in pale yellow prisms, and melts with decomposition at 134° .

The compound $\text{C}_6\text{H}_{10}\text{N}_2\text{O}$ is produced by the action of hydroxylamine on dipropionitrile; it has been described by Hanriot (Abstr., 1892, 79) as amidomethylethylisoxazole, but the author shows cause why it should be regarded as *oximidodipropionitrile*,



Cyanacetone hydrazone, $\text{CN} \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{N} \cdot \text{NHPh}$, is obtained by the action of phenylhydrazine on diacetonitrile in acetic acid; it crystallises in prismatic needles and melts at 97° ; its *hydrochloride* was prepared.

Cyanacetophenone hydrazone, $\text{CN} \cdot \text{CH}_2 \cdot \text{CPh} \cdot \text{N} \cdot \text{NHPh}$, from benzacetodinitrile and phenylhydrazine, crystallises in prismatic needles, and melts at 121° (compare Hanriot, Abstr., 1292, 324). A. G. B.

Amidophosphates. By H. N. STOKES (*Amer. Chem. J.*, 15, 198—214)—*Diphenylic amidophosphate*, $\text{NH}_2 \cdot \text{PO}(\text{OPh})_2$, is prepared by boiling phosphorus oxychloride (1 mol.) with phenol (2 mols.) in a reflux apparatus, and treating the alcoholic solution of the resulting product, a mixture of triphenylic phosphate, diphenylphosphoric chloride, phenylphosphoric dichloride, and unchanged oxychloride, with a slight excess of alcoholic ammonia. The crystalline amidophosphate, mixed with oily phenylic phosphates, separates on the addition of water, and is purified in the usual way. Diphenylic amidophosphate forms brilliant, colourless crystals, melts at 148° , and sublimes at 230° , with partial decomposition into phenol, ammonia, and a non-volatile substance containing phosphorus. *Phenylic hydrogen amidophosphate* is obtained in solution by decomposing *phenylic lead amidophosphate* with hydrogen sulphide. The *ammonium*, *silver*, and *barium* salts are also described. The phenylic hydrogen amido-

phosphate takes up water to form *phenylic hydrogen ammonium phosphate*, which with silver nitrate gives a crystalline precipitate of *phenylic diargentate phosphate*. *Potassium hydrogen amidophosphate* is obtained by hydrolysis of the phenylic salt with potash. The preparation and properties of numerous metallic salts are also described. The silver salt is decomposed on ignition into a stable *silver pyrimidophosphate*, $\text{NH}[\text{PO}(\text{OAg})_2]_2$. Free *amidophosphoric acid* is obtained in solution by passing hydrogen sulphide through an aqueous suspension of the silver salt, and is precipitated by alcohol in colourless, microscopic crystals. It is sweet to the taste, and is not hydrolysed by caustic alkalis. Its alkali hydrogen salts precipitate metallic hydrogen salts from metallic solutions, and its normal alkali salts give normal metallic salts. JN. W.

Alkali Phenoxides. By DE FORCRAND (*Compt. rend.*, 116, 192—194 and 437—439).—The author has prepared and analysed the compound $\text{C}_6\text{H}_5\text{O}\cdot\text{KOH}\cdot\text{H}_2\text{O}$ or $\text{C}_6\text{H}_5\cdot\text{OK}\cdot 2\text{H}_2\text{O}$, obtained in brilliant lamellæ by Roméi's method of mixing and concentrating alcoholic solutions of the two constituents, and also by concentrating mixed aqueous solutions.

The compound $\text{C}_6\text{H}_5\text{O}\cdot\text{NaHO}\cdot 4\text{H}_2\text{O}$ or $\text{C}_6\text{H}_5\cdot\text{ONa}\cdot 5\text{H}_2\text{O}$ is obtained in crystals by concentrating mixed aqueous solutions of the constituents; and the compound $\text{C}_6\text{H}_5\text{O}\cdot\text{NaOH}\cdot 2\text{H}_2\text{O}$ or $\text{C}_6\text{H}_5\cdot\text{ONa}\cdot 3\text{H}_2\text{O}$, by Roméi's method of concentrated mixed alcoholic solutions.

When placed in a dry vacuum for several weeks, all these compounds lose water, and although they do not become completely anhydrous, the composition of the residues agrees much more closely with the formula $\text{C}_6\text{H}_5\text{MO}$ than with the formula $\text{C}_6\text{H}_5\text{O}\cdot\text{MOH}$.

It follows that Roméi's statements are incorrect, and that the so-called hydrated alkali phenates are really hydrates of the phenoxides, the general formula being $\text{C}_6\text{H}_5\text{MO} + x\text{H}_2\text{O}$. This view is supported by their thermochemical behaviour.

The heats of dissolution of the compounds $\text{C}_6\text{H}_5\text{NaO} + 3\text{H}_2\text{O}$, $\text{C}_6\text{H}_5\text{NaO} + 5\text{H}_2\text{O}$, and $\text{C}_6\text{H}_5\text{KO} + 2\text{H}_2\text{O}$ are respectively +0.94 Cal., -4.29 Cal., and +0.12 Cal. If the compounds are regarded as molecular compounds of phenol and the alkali hydroxides, these values would lead to heats of formation much too high for efflorescent hydrates, whereas the numbers calculated on the assumption that the metal has displaced the hydrogen in the hydroxyl group are of the same order of magnitude as in the case of other efflorescent hydrates. This furnishes additional evidence that the true constitution of these compounds is represented by the formula $\text{C}_6\text{H}_5\text{MO} + n\text{H}_2\text{O}$. C. H. B.

Derivatives of Dibromothymol. By F. PELLACANI (*Gazzetta*, 22, ii, 583—586).—*Methyldibromothymol*, $\text{C}_6\text{HMePrBr}_2\cdot\text{OMe}$, may be prepared by the general method from dibromothymol; it is a yellow oil, which does not solidify at -18° .

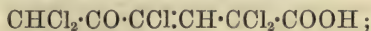
Ethylenedibromothymol, $\text{C}_2\text{H}_4(\text{O}\cdot\text{C}_6\text{HMePrBr}_2)_2$, is obtained by the action of alcoholic potash and ethylenic bromide on dibromothymol;

it forms lustrous needles, melting at 151—153°, and is very soluble in acetic acid or light petroleum, but only sparingly so in alcohol.

Acetyldibromothymol, $C_6HMePrBr_3 \cdot OAc$, is a syrupy, yellow oil, which does not solidify at -18° . *Benzoyldibromothymol* is obtained in minute, lustrous, colourless prisms, melting at 88—90°; it is very soluble in alcohol, light petroleum, or glacial acetic acid.

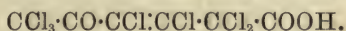
W. J. P.

Action of Chlorine on Phenols. By T. ZINCKE (*Ber.*, 26, 498—512; see also *Abstr.*, 1891, 689; this vol., i, 259).—A further examination of the acid, $C_6Cl_5H_3O_3$, obtained from pentachlororesorcinol, shows that it has the constitution



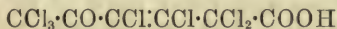
and therefore that pentachlororesorcinol and hexachlororesorcinol are decomposed in a similar way.

Hexachlororesorcinol, when treated with bleaching powder in acetic acid solution, yields an acid of the constitution



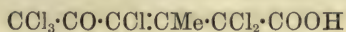
A similar reaction takes place with pentachlororesorcinol, when trichloroacetyltrichlorocrotonic acid, $CCl_3 \cdot CO \cdot CCl : CH \cdot CCl_2 \cdot COOH$, is obtained. In the absence of acetic acid, however, the pentachlororesorcinol is converted into trichloroacetyl- β -chloroacrylic acid, $CCl_3 \cdot CO \cdot CCl : CH \cdot COOH$. The same acid is also obtained by the action of bleaching powder on trichloroacetylchlorocrotonic acid, and on the acid $C_6Cl_5H_3O_3$ obtained from pentachlororesorcinol.

Of the acids $CHCl_2 \cdot CO \cdot CCl : CCl \cdot CCl_2 \cdot COOH$ and



obtained from hexachlororesorcinol, the first is easily converted into the second by the action of bleaching powder; but the second is very stable towards bleaching powder, and when treated with a concentrated solution, is precipitated as calcium salt. In dilute solution, however, it is slowly converted into the acid $CCl_3 \cdot CO \cdot CCl : CCl \cdot COOH$, which, however, cannot be isolated, but decomposes yielding dichloromaleic acid. If, however, the action takes place in acetic acid solution, the compound $CCl_3 \cdot CO \cdot CCl : CCl \cdot CCl_3$ is obtained, and this is identical with the substance obtained by Zincke and v. Lohr from tetrachlorodiketopentene (*Abstr.*, 1892, 1186).

Of the acids $CHCl_2 \cdot CO \cdot CCl : CMe \cdot CCl_2 \cdot COOH$ and



obtained from pentachlororesorcinol, the former is easily converted into the latter by the action of bleaching powder. The latter acid then yields trichloroacetylchloromethylacrylic acid.

The acids containing the group $CCl_2 \cdot COOH$ are not easily converted by bleaching powder into the acid containing one carbon atom less; the group $CCl_2 \cdot COOH$ either withstands the oxidation, or is

converted into CCl_3 . If, however, these acids are first treated with soda, they are converted into $\delta\alpha$ -diketonic acids, and the latter are easily oxidised (see following abstract).

Trichloracetyltrichlorocrotonic acid separates from benzene in short, colourless crystals, and melts at 96° . When treated with sodium hydroxide, it yields chloroform and an oily, uncharacteristic acid. With sodium carbonate, very little chloroform is formed, and an oily acid is obtained, which, on heating, yields the pentene derivative $\text{C}_5\text{Cl}_3\text{HO}_2$, and when oxidised with bleaching powder is converted into dichloracetyl- β -chloracrylic acid. When dissolved in acetic acid, and subjected to steam distillation, it is converted into the ketone $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}\cdot\text{CH}\cdot\text{CHCl}_2$. This is a heavy, highly-refractive, yellow oil, which has a characteristic odour resembling that of camphor, boils at $122\text{--}124^\circ$ under 18–20 mm. pressure, and when treated with alkali, yields chloroform and an oily acid.

Trichloracetyl- β -chloracrylic acid crystallises in white, satiny leaflets, and melts at 126° . The *methyl*ic salt crystallises in colourless tablets, and melts at 71° . When allowed to remain with excess of 10 per cent. soda for 24 hours, it is converted into chloroform and chloromaleic acid, $\text{COOH}\cdot\text{CH}\cdot\text{CCl}\cdot\text{COOH}$; this crystallises in white needles, sinters at $95\text{--}96^\circ$, and melts at 108° . The *potassium hydrogen* salt crystallises in rosettes of colourless needles. The *barium* salt, $\text{C}_2\text{HCl}\cdot\text{C}(\text{COO})_2\cdot\text{Ba}, 2\text{H}_2\text{O}$, crystallises in white crusts. The

author has also prepared chloromaleic acid from chlorofumaric acid, and finds that it is identical with the above acid.

Perchloracetylacrylic acid, $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}\cdot\text{CCl}\cdot\text{COOH}$, is obtained when the acid $\text{C}_6\text{HCl}_7\text{O}_3$, from hexachlororesorcinol is treated with sodium carbonate, and then cautiously oxidised with bleaching powder. It crystallises with water, melts at 50° , when dry melts at $83\text{--}84^\circ$, and is identical with the perchloracetylacrylic acid described by Zincke and v. Lohr (Abstr., 1892, 1186).

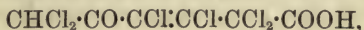
Trichloracetylchloromethylacrylic acid, $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}\cdot\text{CMe}\cdot\text{COOH}$, is best obtained by treating the acid $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}\cdot\text{CMe}\cdot\text{CCl}_2\cdot\text{COOH}$ (from pentachlororcinol) with sodium carbonate, and then oxidising with bleaching powder. It crystallises in colourless needles or prisms, melts at 135° , and when treated with sodium hydroxide yields chloroform and chlorocitraconic acid.

E. C. R.

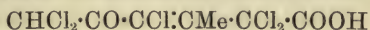
Conversion of the Ketochlorides of Resorcinol and Orcinol into Pentene Derivatives. By T. ZINCKE and O. FUCHS (*Ber.*, 26, 513–521; compare this vol., i, 259).—The chlorinated δ -ketonic acids obtained from the ketochlorides of resorcinol and orcinol are converted into chlorine derivatives of metadikopentene by heating them with 10–15 parts of concentrated sulphuric acid, pouring the product on to ice, and then subjecting it to steam distillation. The diketopentenes are also obtained by treating the ketonic acids with sodium carbonate, allowing the faintly alkaline mixture to remain for a short time, then acidifying with hydrochloric acid and extracting with ether. On evaporating the ethereal solution, a viscid, yellow oil is obtained, which is a $\delta\alpha$ -diketonic acid; this,

when cautiously heated on the water-bath, decomposes and yields the diketopentene.

The acid, $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}_2\cdot\text{CHCl}\cdot\text{CCl}_2\cdot\text{COOH}$, from pentachlororesorcinol, is easily converted into tetrachlorodiketopentene by boiling with water, but with soda, it yields chloroform and pentachloroglutaric acid. The other acids, with the exception of the acid



which yields perchloroketoidene, require to be treated as described above, but bye-products are always obtained. Thus acids containing the group $\text{CCl}_3\cdot\text{CO}$ yield chloroform, and the acid



yields the compound $\text{C}_5\text{Cl}_3\text{MeO}$.

Dichlorodiketopentene, $\begin{array}{c} \text{CCl}\cdot\text{CO} \\ || \\ \text{CH}\cdot\text{CO} \end{array} > \text{CHCl}$, crystallises in white, silky needles, melts at 89° , sublimes in slender needles, boils without decomposition, and when warm has a characteristic odour. It is not attacked by sodium carbonate, and yields a brownish solution with sodium hydroxide. When treated with bleaching powder in acetic acid solution, it yields trichloroacetyl- β -chloroacrylic acid, $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}\cdot\text{CH}\cdot\text{COOH}$ (m. p. 126°). The *azine*, $\text{C}_{11}\text{H}_7\text{ClN}_2\text{O}$, obtained by warming an alcoholic solution of the diketone with orthophenylenediamine, crystallises from benzene in red needles, which sinter at 160° , and melt at 170° with decomposition, and from alcohol or acetic acid in slender, yellow needles, which melt at $160\text{--}165^\circ$ with decomposition; both modifications give with soda a sparingly soluble, yellow salt, and with hydrochloric acid a yellow precipitate.

Unsymmetrical trichlorodiketopentene, $\begin{array}{c} \text{CCl}\cdot\text{CO} \\ || \\ \text{CH}\cdot\text{CO} \end{array} > \text{CCl}_2$, crystallises in stout, colourless needles, melts at 69° , is volatile with steam, is not attacked by sodium carbonate, but is decomposed by sodium hydroxide, and yields resins with orthophenylenediamine.

Symmetrical trichlorodiketopentene, $\begin{array}{c} \text{CCl}\cdot\text{CO} \\ || \\ \text{CCl}\cdot\text{CO} \end{array} > \text{CHCl}$, crystallises in colourless needles, melts at $49\text{--}50^\circ$, and closely resembles the preceding compound, but with orthophenylenediamine, yields a compound which crystallises in beautiful red needles, blackens at 185° , and melts at $190\text{--}195^\circ$.

Dichlorodiketomethylpentene, $\begin{array}{c} \text{CCl}\cdot\text{CO} \\ || \\ \text{CMe}\cdot\text{CO} \end{array} > \text{CHCl}$ (see also this vol., i, 260), crystallises in thin, colourless tablets, and melts at 81° . The *azine* crystallises in slender, yellow needles, and melts at 186° .

Trichlorodiketomethylpentene, $\begin{array}{c} \text{CCl}\cdot\text{CO} \\ || \\ \text{CMe}\cdot\text{CO} \end{array} > \text{CCl}_2$, crystallises in short, colourless needles or prisms, melts at $64\text{--}65^\circ$, and yields resins with orthophenylenediamine.

Perchloroketoindene, $C_6Cl_4 < \begin{smallmatrix} CO \\ CCl \end{smallmatrix} > CCl$, is obtained by dissolving the acid $CHCl_2 \cdot CO \cdot CCl : CCl : CCl_2 \cdot COOH$ in sodium carbonate, and after allowing the mixture to remain for a time, filtering off the precipitate which is formed and adding hydrochloric acid to the clear liquid. The precipitate thus obtained crystallises in yellow plates, melts at 148° , and is identical with the perchloroketoindene described by Zincke and Günther (this vol., i, 344).
E. C. R.

Creosotes and Guaiacol. By A. BÉHAL and E. CHOAY (*Compt. rend.*, 116, 197—200).—Official creosotes are mixtures of very variable composition. Their analysis is based on the following facts. (1) When a current of hydrogen bromide is passed into a heated mixture of creosote under ordinary pressure, the methyl derivatives are completely demethylated. (2) Phenols are volatile in water vapour, whilst polyphenols are practically non-volatile. (3) From the aqueous solution, ether completely removes catechol and homocatechol, together with any traces of phenols that may be left. (4) Catechol and homocatechol can be separated with considerable accuracy by means of benzene.

Guaiacol.—Commercial guaiacol is very impure, and rarely contains more than 50 per cent. of the pure compound. It is generally described as a liquid, but the values attached to its boiling point and sp. gr. are very various.

In order to obtain the pure compound, 58 grams of sodium is dissolved in methyl alcohol, mixed with a solution of 270 grams of catechol in methyl alcohol, and heated at 120 — 130° with excess of methylic iodide in an autoclave. After distilling off the alcohol, the product is distilled in a current of steam, the guaiacol dissolved in sodium hydroxide solution, and agitated with ether to remove veratrol. The guaiacol is liberated by means of hydrochloric acid, distilled in a current of steam, and afterwards fractionated. The portion boiling at 205 — 207° is cooled by means of methylic chloride, when the pure guaiacol crystallises. It is a white, solid compound which crystallises readily in uniaxial dihexagonal prisms; it melts at 28.5° , and boils at 205.1° . When melted, guaiacol remains indefinitely in superfusion. Its sp. gr. at $0^\circ = 1.1534$, and at $15^\circ 1.143$. It dissolves in most organic solvents, including anhydrous glycerol, but it does not dissolve in official glycerol. If, however, the latter is heated, the guaiacol dissolves readily, but separates as an oil on cooling. Guaiacol crystallises readily from light petroleum. It has a sweet and intensely astringent taste, but does not attack the mucous membrane.
C. H. B.

Additive Products of Benzoquinone and Toluquinone. By T. H. CLARK (*Amer. Chem. J.*, 14, 553—576).—Contains the experimental data upon which some conclusions already published by Nef (Abstr., 1891, 1348; compare also 1892, 1272) are based, and an account of some further experiments. Five additive products of benzoquinone have so far been obtained; a di- and a tetra-bromide, a

di- and a tetra-chloride, and a dichloride-dibromide. These are stable, especially the chlorine derivatives. The dichloride and dibromide have a faint, quinone-like odour, are light coloured, and dissolve moderately in organic solvents, and without change in fuming nitric acid. The other three are colourless, inodorous, and very sparingly soluble in organic solvents; they dissolve with difficulty and without change in warm fuming nitric acid. All five are instantly decomposed by dilute aqueous soda; they all lose hydrogen haloid (1 or 2 mols.) when their alcoholic solutions are warmed, and form one, or two isomeric, halogen-substituted benzoquinones. When reduced with zinc and acetic acid, they all yield quinol. Toluquinone forms a dibromide and a dichloride [$\text{Me} : \text{O}_2 : \text{Br}_2$ (or Cl_2) = 6 : 1 : 4 : 2 : 3], but no tetrahalogen additive product. These products closely resemble the corresponding benzoquinone derivatives. When reduced with zinc and acetic acid, they yield toluquinol. When their alcoholic solutions are boiled, they lose halogen hydride, and form mixtures of meta- and para-chloro- (or bromo-) toluquinone. This shows that the halogen atoms must have been added on in the 2 : 3-, and not in the 5 : 6-, positions. That the addition of 2 halogen atoms always takes place in ortho-positions is proved by the fact that benzoquinone dichloride-dibromide, formed by the successive addition of 2Cl and 2Br, yields, when warmed in alcoholic solution, a mixture of meta- and para-chlorobromoquinone [$\text{O}_2 : \text{Cl} : \text{Br} = 1 : 4 : 2 : 6$ and $1 : 4 : 6 : 3$] in about equal proportions.

The corrected melting points of the chlorine additive products are given, and differ slightly from those previously quoted. The dichloride melts at 146° , and then decomposes at about 185° , but the solid sublimes without decomposition; it was obtained in colourless, transparent plates by recrystallisation from acetic acid. The tetrachloride darkens at about 185° , and usually melts at 226° , but often sublimes without melting at 236° . The dichloride-dibromide melts at $202\text{--}203^\circ$ with decomposition, part subliming at the same time. Incidentally it is mentioned that a good method of preparing the quinones is to dissolve quinol (or orthotoluidine) in dilute sulphuric acid, add manganese dioxide, distil the mixture with steam, cool the distillate with ice and salt, and filter off the solid benzo- (or tolu-) quinone.

Three substances previously mentioned (Abstr., 1891, 1348) are also more accurately described. *Chlorobromaniline* [$\text{NH}_2 : \text{Cl} : \text{Br} = 1 : 2 : 5$] crystallises from water in fine, silky, white needles melting at $44\cdot5^\circ$. Its *hydrochloride*, $\text{C}_6\text{H}_5\text{ClBrN}\cdot\text{HCl} + \text{H}_2\text{O}$, melting at 196° , and *sulphate*, $(\text{C}_6\text{H}_5\text{ClBrN})_2\cdot\text{H}_2\text{SO}_4$, were prepared. *Bromochloropara-nitrophenol* [$\text{OH} : \text{Cl} : \text{NO}_2 : \text{Br} = 1 : 2 : 4 : 6$] forms white crystals melting at $139\cdot5^\circ$. When reduced with tin and hydrochloric acid, it yielded *bromochloroparamidophenol stannochloride* as long, silky, white needles melting at 228° . The sulphate forms white, silky needles melting at 221° , and the base itself long, colourless needles, but neither of these was obtained quite pure.

Toluquinone dichloride, obtained by passing chlorine into a chloroform solution of the quincne, is a white, crystalline substance which melts at $135\text{--}136^\circ$, and then decomposes at about 164° , but can also

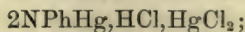
be sublimed unchanged. The *dibromide* forms pale yellow crystals, melting at 61—62°, and subliming at a higher temperature.

The action of hydrochloric acid on benzoquinone does not give rise to a hydrochloride. When the dry gas is passed into a chloroform solution of the quinone, the following reactions occur; the hydrochloric acid first reduces the quinone, setting free chlorine, which remains dissolved, and forming quinol, which at once combines with unchanged quinone to form quinhydrone; the latter is then attacked by more hydrochloric acid, which reduces the quinone part of it to quinol, setting more chlorine free. The whole of the chlorine set free now attacks the quinol which has been formed, and converts it into chloroquinol, which is obtained as the sole final product of the reaction. In the case of toluquinone, the reaction is similar, and a mixture of much *para*- with some *meta*-chlorotoluquinol is obtained.

Quinhydrone, when heated in chloroform solution with dry gaseous hydrogen chloride, yields a mixture of quinol and chloroquinol in molecular proportion. A *chloroquinhydrone*, $C_6H_4(OH)_2.C_6H_3ClO_2$, may be obtained by mixing ethereal solutions of quinol and chloroquinone; it is readily decomposed by solvents. Quinone and chloroquinol do not, however, yield a similar compound; as a result of mixing their ethereal solutions, much chloroquinol and quinone, and some quinol and chloroquinone, were obtained. C. F. B.

Some Derivatives of Chloranil. By H. S. GRINDLEY and C. L. JACKSON (*Ber.*, 26, 397—398).—If chloranil is treated with sodium phenoxide, *diphenoxydichloroquinone*, $C_6Cl_2O_2(OPh)_2$, is obtained in red needles melting at 242°. When reduced with hydriodic acid, this substance yields the corresponding *quinol* in white needles melting at 197°. When treated with ethylic sodiomalonate, a blue precipitate is obtained, changing to yellow when the solution is acidified. The yellow substance, which crystallises in needles, is a molecular compound, $C_6Cl_2O_2.2CH(COOEt)_2$; it is reduced by hydriodic acid to a white substance, probably the quinol. The blue substance is its *sodium* derivative, $C_6Cl_2O_2.2CNa(COOEt)_2$. C. F. B.

Mercuranilido-compounds. By A. PICCININI and G. RUSPAGGIARI (*Gazzetta*, 22, ii, 604—610).—The double hydrochloride of mercurio-phenylamine and aniline prepared by Pesci (*Abstr.*, 1892, 1448) was stated by him to be identical with a compound obtained in another way by Gerhardt and by Schiff. The authors now establish the identity of the products from the two sources, showing that they yield the same substance when heated with water; this remains as a yellowish, insoluble powder having the composition



on treatment with hydrogen sulphide, it yields aniline hydrochloride, mercuric sulphide, and hydrochloric acid.

The substance prepared by Schiff, by the action of aniline on mercuric acetate solution, yields mercurio-phenylamine acetate when treated with water; it must therefore be considered as a double

acetate of mercurio-phenylamine and aniline having the composition $\text{NH}_2\text{Ph}, \text{C}_2\text{H}_4\text{O}_2, \text{NPhHg}, \text{C}_2\text{H}_4\text{O}_2$.

A substance to which the formula $2\text{NH}_2\text{Ph}, \text{Hg}(\text{NO}_3)_2$ has been assigned, is obtained by the action of aniline on mercuric nitrate in aqueous solution; on treating it with boiling water, a compound of the composition $\text{N}_2\text{H}_2\text{Ph}_2, \text{Hg}_2(\text{NO}_3)_2$ is supposed to be formed. The authors find, however, that the former substance should be considered as a double salt of aniline and mercurio-phenylamine, as on boiling with water it yields mercurio-phenylamine nitrate; they conclude, further, that all the supposed mercuranilido-compounds are really double salts of aniline and mercurio-phenylamine. W. J. P.

Direct Conversion of Aniline into Nitrobenzene. By PRUD'HOMME (*Bull. Soc. Chim.* [3], 7, 621—623; compare Bamberger and Meimberg, next abstract).—When a mixture of aniline, hydrogen peroxide, and water, with or without the addition of magnesia, is heated in a reflux apparatus, the principal products are paramidophenol, azobenzene, azoxybenzene, and nitrobenzene.

Azobenzene and azoxybenzene are not converted into nitrobenzene when similarly treated with hydrogen peroxide. A. R. L.

Direct Conversion of Aniline into Nitrobenzene. By E. BAMBERGER and F. MEIMBERG (*Ber.*, 26, 496—497; compare Prud'homme, preceding abstract).—When potassium permanganate (120 grams) dissolved in water (3 litres) is gradually dropped into a solution of aniline (8 grams) in water (360 grams) at 0° , the mixture being kept in agitation for 8—9 hours, and filtered, ether extracts a brown oil. On distilling the latter in a current of steam, nitrobenzene and azobenzene (but no nitrosobenzene) pass over, and an unknown compound melting at 226° remains. The amounts of the products are small.

By reducing an alkaline solution of diazobenzene with stannous oxide at -10° , hydrazobenzene and phenylhydrazine are formed.

A. R. L.

Action of Phosphorus Oxychloride and of Phosphorus Thiochloride on Aromatic Amines. By P. RUDERT (*Ber.*, 26, 565—575).—*Phosphoric orthotoluidide*, $\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_3$, is formed by the action of phosphorus oxychloride on orthotoluidine. It crystallises in colourless, or reddish, needles or plates, melts at 225° , is decomposed by boiling concentrated hydrochloric acid or soda, and is very readily acted on by oxidising agents. The *bromo-derivative*, $\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_3\text{MeBr})_3$, crystallises in slender, almost colourless needles, and melts at 253° . The *nitro-derivative*, $\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2)_3$, is a pale yellow, crystalline powder, but it was not obtained in a pure condition.

Diorthotoluidophosphoric acid, $\text{OH}\cdot\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$, is obtained when orthotoluidine is treated with excess of phosphorus oxychloride; it is a colourless, crystalline powder, melts at 95° , and is decomposed into toluidine and phosphoric acid by hot concentrated hydrochloric acid. The *sodium* salt crystallises in colourless needles. The *barium* and *silver* salts crystallise in needles.

Thiophosphoric orthotoluidide, $\text{PS}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_3$, can be obtained by treating orthotoluidine with phosphorus thiochloride; it crystallises in colourless needles, melts at $134\cdot5^\circ$, and is decomposed by nitric acid, bromine, and boiling concentrated hydrochloric acid.

Phosphoric paratoluidide, $\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_3$, crystallises in colourless prisms, which belong to the triclinic system, and become opaque on keeping, probably owing to a change in crystalline form; it melts at 192° and is only slowly acted on by hot concentrated hydrochloric acid and by oxidising agents. The *bromo-derivative*, $\text{PO}(\text{NH}\cdot\text{C}_6\text{HMeBr})_3$, is formed when phosphoric paratoluidide is treated with bromine in glacial acetic acid solution until a permanent coloration is produced and the mixture then warmed; it crystallises in lustrous, colourless needles, turns brown at about 100° , and melts at about 180° . The *bromo-derivative*, $\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_3\text{MeBr})_3$, is produced when the preceding compound is boiled with glacial acetic acid; it crystallises in very slender, colourless needles, melts at 221° , and is decomposed by nitric acid. The *nitro-derivative*, $\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2)_3$, crystallises in small, lemon-yellow needles, melts at 247° , and explodes when heated more strongly.

Diparatoluidophosphoric acid, $\text{OH}\cdot\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$, is a crystalline, colourless powder melting at 124° . The *barium* and silver salts crystallise in colourless needles.

Thiophosphoric paratoluidide, $\text{PS}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_3$, crystallises in colourless needles, melts at 185° , and is converted into derivatives of phosphoric paratoluidide on treatment with bromine or with nitric acid.

Phosphoric α -naphthalide, $\text{PO}(\text{NH}\cdot\text{C}_{10}\text{H}_7)_3$, prepared by treating α -naphthylamine with phosphorus oxychloride, crystallises in colourless needles, melts at 216° , and is decomposed by hot concentrated hydrochloric acid; when excess of phosphorus oxychloride is used in the above reaction, *dinaphthylamidophosphoric acid*, $\text{OH}\cdot\text{PO}(\text{NH}\cdot\text{C}_{10}\text{H}_7)_2$, is formed, and can be isolated in the form of a brownish, crystalline powder melting at 197° .

Phosphoric β -naphthalide, $\text{PO}(\text{NH}\cdot\text{C}_{10}\text{H}_7)_3$, crystallises in colourless plates, and melts at 170° ; *dinaphthylamidophosphoric acid*, prepared from β -naphthylamine, is a light orange powder, and melts at 150° .

Phosphoric ethylanilide, $\text{PO}(\text{NEtPh})_3$, can be obtained by heating ethylaniline with phosphorus oxychloride; it crystallises in slender, colourless needles, and melts at 149° . F. S. K.

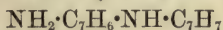
Oxidation Products of Alkyl Derivatives of Orthodiamines.

By F. KEHRMANN and J. MESSINGER (*Ber.*, 26, 599—600).—This paper is purely controversial, being a reply to Fischer and Heiler (this vol., i, 266). F. S. K.

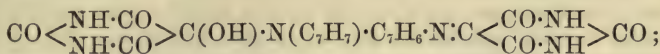
Interaction of Orthamidoditolylamine and Alloxan Derivatives. By O. KÜHLING (*Ber.*, 26, 540—545).—The author has previously shown that orthodiamines react with alloxan and its derivatives with formation of azines, and has now investigated the action of orthodiamines in which a hydrocarbon radicle is substituted for one of the hydrogen atoms of the amido-group, in order to ascertain whether substances corresponding to Witt's azonium.

bases are formed. The results obtained show that the reaction in this case proceeds in a different manner.

When alloxan is mixed with orthamidoditolyamine,



(Abstr., 1892, 853), in alcoholic solution and allowed to remain at the ordinary temperature, only the central carbonyl group enters into the reaction, with formation of *alloxanylorthamidoditolyamine*, $\text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{C}_7\text{H}_6 \cdot \text{N} : \text{C} < \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} > \text{CO}$, which forms glittering, yellow prisms, melts with decomposition at 252° , and dissolves in concentrated sulphuric acid with a deep red colour. If the alcoholic solution of alloxan and orthamidoditolyamine be boiled with an excess of fuming hydrochloric acid, a second molecule of alloxan enters into combination without elimination of water, forming *dialloxanylorthamidoditolyamine*,



it crystallises in very small, pointed needles, blackens at 300° , and is scarcely soluble in the common solvents, but readily dissolves in solutions of the alkalis and their carbonates; none of its salts could, however, be isolated. It dissolves in concentrated sulphuric acid with a deep blue colour, which, on dilution, passes through red to yellow.

Dimethylalloxan yields with orthamidoditolyamine two derivatives which correspond in properties with their lower homologues.

H. G. C.

Decomposition of Diazo-compounds. By I. REMSEN and P. J. DASHIELL (*Amer. Chem. J.*, 15, 105—125; compare Abstr., 1887, 136; 1888, 268; 1889, 975).—It has already been noted (Abstr., 1887, 136) that the chief product of the action of alcohol on paradiazotolueneorthosulphonic acid is not tolueneorthosulphonic acid, but ethoxytolueneorthosulphonic acid, and that the higher the pressure, the larger the proportion of the ethoxy-derivative formed. The authors have further studied this reaction from three points of view, as follows:—(1) The pressure was constant (300 mm.) and the strength of alcohol varied. The presence of small quantities of water in the alcohol has little influence on the course of the reaction in the decomposition of the diazo-compound. The presence of more than 15 per cent. of water gives rise to other reactions than those involved in the formation of toluenesulphonic acid and ethoxytoluenesulphonic acid. Typical figures from which these conclusions may be drawn are:—

Per cent. alcohol	Absolute	95.0	90.0	85.0
Per cent. of ethoxy-product..	43.4	35.8	47.7	40.9

The decomposition is more rapid in dilute alcohol. (2) The alcohol was of constant strength (absolute) and the pressure varied. The following figures were obtained.

Pressure in mm...	120	210	300	400	500	600	700	800
Ethoxy - product, per cent,	37.2	40.6	43.4	48.7	52.8	57.7	63.2	69.8

The curve embodying these results approximates very nearly to a parabola. The experiments were conducted in a flask provided with a valve, weighted to lift at the desired pressure, and a manometer; the temperature of the flask was quickly raised until the manometer indicated the desired pressure [which must therefore be in excess of the barometric pressure, although this is not specifically stated.—ABTRACTOR]. (3) The influence of temperature. The temperature of the above experiments would be that at which the alcohol boils under the pressure maintained. When the pressure was exerted by nitrogen, it was found that for decomposition at any given pressure, a definite temperature is necessary, and this temperature lies very near the point at which the alcohol boils at that pressure. It thus becomes uncertain whether the regular differences noted in the experiments under the various conditions are to be ascribed to the influence of temperature or pressure.

The separation of the tolueneorthosulphonic acid and ethoxytoluene-orthosulphonic acid was effected by means of their barium salts, the former of which is but little soluble in boiling alcohol.

A. G. B.

Behaviour of Diazobenzene towards Potassium Ferricyanide.

By E. BAMBERGER and L. STORCH (*Ber.*, 26, 471—481).—*Nitrosobenzene*, $C_6H_5 \cdot NO$, is obtained by cautiously running a freshly prepared solution of diazobenzene chloride into an alkaline solution of potassium ferricyanide, and allowing the mixture to remain for 70—80 hours at 0° . The compound forms colourless, translucent prisms belonging probably to the monoclinic system, melts at 67.5 — 68° to an emerald-green liquid which subsequently resolidifies to colourless crystals. It is volatile with steam and other vapours, has an odour recalling that of the ethereal thiocarbimides or, still more, that of cyanic acid, and yields green solutions; indeed it has already been obtained in solution (see Baeyer, this Journal, 1875, 452; Aronheim, *Abstr.*, 1879, 651).

When the above-mentioned mixture is allowed to remain longer than 70—80 hours, a precipitate separates, which is collected and distilled with steam, when nitrosobenzene and azobenzene pass over. A further quantity of nitrosobenzene, together with nitrobenzene and diphenyl, is extracted by ether from the filtrate; the latter is then saturated with carbonic anhydride, and cautiously treated at 0° with sufficient 30 per cent. sulphuric acid to cause it to just turn Congo paper blue. Ether extracts from this solution *benzenediazoic acid*, $C_6H_5 \cdot N_2O_2H$, a compound melting at 46 — 46.5° and exploding at 97 — 98° (see also next abstract).

The solution freed from benzenediazoic acid is treated with 50 per cent. sulphuric acid, and the precipitate, after drying on a tile, dissolved in alcohol and ether added. The precipitate which falls is dissolved in water and the solution neutralised with barium carbonate,

when barium ferrocyanide is obtained. After removing the latter, barium phenylferrocyanide, $\text{Ba}_3(\text{PhFeC}_6\text{N}_6)_2 + 2\text{H}_2\text{O}$, is isolated. A solution of this salt gives off the odour of isonitriles on being warmed with alkali, and yields precipitates with the salts of those metals which are precipitated by potassium ferrocyanide. A. R. L.

Behaviour of Diazobenzene towards Potassium Permanganate. By E. BAMBERGER and K. LANDSTEINER (*Ber.*, 26, 482—495).—In studying the action of potassium permanganate on diazobenzene, it is necessary to employ a large excess of alkali, and to cool well. When a solution of a salt of diazobenzene (from 20 grams of aniline) is mixed with a cooled 20 per cent. solution of potassium hydroxide (60 grams), potassium permanganate (34 grams) dissolved in water (850 c.c.) added, and the mixture set aside at 0° for two days, benzenediazoic acid (last abstract) is the chief product, but there is also formed nitrosobenzene, nitrobenzene, diphenyl, azobenzene, and phenylisonitrile. The following salts of benzenediazoic acid are described. The *silver* salt is an explosive crystalline precipitate, stable towards light; the *lead* salt resembles it, and is not very soluble in hot water; the *barium* salt crystallises with 2 mols. H_2O ; and the *potassium* salt forms radiating groups of needles; the *phenylhydrazine* salt melts at $94.5\text{--}95^\circ$.

When the acid is heated in an oil-bath, as soon as the temperature rises to $97\text{--}98^\circ$, decomposition suddenly takes place, the products being nitrogen, carbonic and nitrous anhydrides, nitrosobenzene, ortho- and para-nitraniline, and ortho- and para-nitrophenol. The acid is also decomposed by boiling its solution in toluene. Mineral acids decompose it at 0° , yielding principally orthonitraniline; it also decomposes when boiled with water. It is, on the other hand, very stable towards alkalis, but on being heated with aqueous potash at $280\text{--}290^\circ$, aniline distils over. On reduction with zinc-dust and acetic acid, diazobenzene is the main product, but aniline, ammonia, diphenyl, and perhaps azobenzene are also formed. The non-formation of phenylhydrazine, on reduction, leads the authors to the view that benzenediazoic acid is constituted similarly to Franchimont's nitrosamines, but although, of the two tautomeric formulæ proposed, namely, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NO}_2$ and $\text{C}_6\text{H}_5\cdot\text{N}:\text{NOOH}$, their results favour the first, neither can be regarded as established. The authors also consider that their results prove that diazobenzene is a tautomeric compound which can equally well be represented by either of the formulæ $\text{C}_6\text{H}_5\cdot\text{N}:\text{NOH}$ or $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NO}$. A. R. L.

Reduction Products of Azo-compounds. II. By P. JACOBSON, F. C. FERTSCH, and W. FISCHER (*Ber.*, 26, 681—688). **III.** By P. JACOBSON, F. HENRICH, and J. KLEIN (*Ber.*, 26, 688—698). **IV.** By P. JACOBSON (*Ber.*, 26, 699—705; see also *Abstr.*, 1892, 839).—The base obtained as the chief product of the reduction of benzeneazophenetoil with stannous chloride and hydrochloric acid, and obtained by Bohn from benzenehydrazophenetoil, has been subjected to a further examination. Of the two possible formulæ, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ [$\text{NH}:\text{NH}_2 = 1:2$], orthamidophenylpara-

phenetidine, and $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OEt})\text{NHPH}$ [$\text{NHPH} : \text{NH}_2 : \text{OEt} = 1:2:5$], metanilidoparaphenetidine, the latter is proved to be the correct one, by comparing the properties of the base with these two compounds, synthetically prepared.

When the base is heated in a sealed tube with hydrochloric acid at $120\text{--}130^\circ$ for three hours, it yields aniline, ethyl chloride, and ammonia.

Orthamidophenylparaphenetidine is easily obtained by heating ortho-bromonitrobenzene with phenetidine and alcohol in a sealed tube at 180° , and then reducing the nitrophenylphenetidine thus obtained with stannous chloride and hydrochloric acid. *Orthonitrophenylparaphenetidine*, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, forms beautiful orange-yellow, prismatic crystals, and melts at 84° .

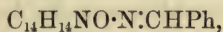
Metanilidoparaphenetidine is obtained from 2:5-nitrochlorodiphenylamine. When this nitro-compound is heated with sodium ethoxide and alcohol in a sealed tube at 120° , and the product diluted with water, about 15 per cent. of *metanilidoparanitrophenetol* is obtained; this crystallises in beautiful orange-yellow needles, and melts at $106\text{--}106.5^\circ$. A further addition of water causes a precipitate of *dianilidoazoxyphenetol*, $\text{ON}_2[\text{C}_6\text{H}_3(\text{OEt})\cdot\text{NHPH}]_2$, which crystallises in bright golden-yellow needles, and melts at 125° . Finally, the alkaline alcoholic solution in which the addition of water causes no further precipitate contains *metanilidoparanitrophenol*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{NHPH}$; this is the main product of the reaction, and is precipitated on acidifying with sulphuric acid. It crystallises from alcohol in nodular aggregates, from benzene in lustrous leaflets, melts at 165° , and is easily converted into metanilidoparanitrophenetol by boiling with ethylic bromide and sodium ethoxide. When heated with alcoholic ammonium sulphide at 120° , it yields metanilidoparaphenetidine.

Orthamidophenylparaphenetidine and metanilidoparaphenetidine, as also their hydrochlorides, cannot be distinguished from each other; both crystallise in colourless needles which turn violet on exposure to air, and melt at 95° . The hydrochlorides are easily soluble in water, and are precipitated by hydrochloric acid. They are distinguished by the following properties:—*Orthamidophenylparaphenetidine* gives, with a small quantity of ferric chloride, an intense red coloration, and a brown precipitate on the addition of a further quantity of ferric chloride; the colour is unaltered by hydrochloric acid. The *azimide* crystallises from petroleum in spears, and melts at $95\text{--}96^\circ$. The *methenyl compound* crystallises in tablets, and melts at $79\text{--}80^\circ$. The *azonium base* obtained by condensation with benzile sinters at 170° , melts at $175\text{--}180^\circ$, and yields a dark reddish-brown solution with concentrated sulphuric acid. When heated with carbon bisulphide on the water-bath, it remains unaltered, but when heated under pressure at 150° , it yields a compound which crystallises in small tablets, and melts at 227° . Metanilidoparaphenetidine, on the other hand, gives a reddish-violet coloration with ferric chloride which turns bluish-violet on the addition of hydrochloric acid. The *azimide* crystallises from petroleum in plates, and melts at 107° . The *methenyl compound* crystallises in plates, and melts at 77° . The *azonium base* melts at

144—147°, and then solidifies and melts again at 164—165°, and yields a bright red solution with concentrated sulphuric acid. When heated with carbon bisulphide on the water-bath, it is easily converted into a product which crystallises in long, white needles, and melts at 228°.

The reduction of benzenazophenetoil results in the production of about 50 per cent. of metanilidoparaphenetidine, 25 per cent. of aniline and paraphenetidine; and, besides this, about 5 per cent. of parethoxyparamidodiphenylamine has been isolated from the product.

Parethoxyparamidodiphenylamine is obtained as the stannochloride when the mother liquors of the preceding base are allowed to remain some time. The *free base* crystallises in beautiful colourless needles, darkens quickly on exposure to air, and melts at 98—99·5°. It gives an intense blue coloration with ferric chloride which disappears on the addition of concentrated hydrochloric acid; with a small quantity of nitrous acid, a dark violet coloration; and with more nitrous acid, a clear, golden-yellow solution. The *hydrochloride*, $C_{14}H_{16}N_2O \cdot HCl$, crystallises in colourless needles, and is not precipitated by hydrochloric acid. The *monacetyl derivative*, obtained by boiling the base with glacial acetic acid, crystallises in slender, interlacing needles, and melts at 134°. The *diacetyl derivative* crystallises in right-angled plates, and melts at 175—176°. The *diazochloride*, $C_{14}H_{14}N_3OCl$, crystallises in bright yellow leaflets, is very stable, and in small quantities may be recrystallised from hot water without decomposition. The *thiocarbamide*, obtained by heating an alcoholic solution of the base with carbon bisulphide, crystallises in yellowish-grey needles, and melts at 155—156°. The *monobenzylidene derivative*,



melts at 109—110°.

The base has also been prepared synthetically from parahydroxydiphenylamine; both methods of preparation yield identical compounds.

Parahydroxydiphenylamine is obtained by Calm's method by heating a mixture of quinol, aniline, and calcium chloride at 250—260° (*Ber.*, 16, 2799; 17, 2431).

Parethoxydiphenylamine crystallises in long, flat, colourless needles, melts at 73—74°, boils at 348°, and dissolves in concentrated hydrochloric acid, yielding a hydrochloride which is easily decomposed by water. The *nitrosoamine* crystallises in short, transparent prisms, and melts at 73—75°.

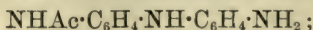
Parethoxyparanitrosodiphenylamine, $OEt \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot NO$, obtained by molecular change from the above nitrosoamine, crystallises in beautiful green leaflets, and melts at 150—155°. When reduced with alcoholic ammonium sulphide, it yields parethoxyparamidodiphenylamine.

The preceding researches show that when benzenazophenetoil is reduced with a warm mixture of stannous chloride and hydrochloric acid, about 25 per cent. of the azo-compound is resolved into aniline and paraphenetidine; the greater part, however, is reduced to the

hydrazo-compound, and this undergoes molecular change yielding two compounds, derivatives of ortho- and of para-amidodiphenylamine. It is proposed to call this reaction the *semidine reaction*, and to designate the orthamidodiphenylamine bases thus obtained by the name *orthosemidines*; the paramidodiphenylamine bases by the name *parasemidines*.

An examination of the behaviour of the five isomeric monomethyl derivatives of benzeneazophenetoil, when treated with a warm mixture of stannous chloride and hydrochloric acid, has led to the following results:—Benzeneazooorthocresetoil and metatoluenazophenetoil behave in the same way as benzeneazophenetoil, and yield as chief products an orthosemidine, a small quantity of a parasemidine, and are partly resolved into their constituents. Benzeneazometacresetoil and orthotoluenazophenetoil are partly resolved into their constituents, but the chief product is a parasemidine, and no orthosemidine is formed. The production of an orthosemidine is not, however, impossible, but would lead to the production of a compound containing three substituents in the ortho-position to one another. Paratoluenazophenetoil is completely split up into paratoluidine and paraphenetidine, although the hydrazo-compound obtained from it by reduction with ammonium sulphide, when treated, in alcoholic solution, with stannous chloride and hydrochloric acid, gives a good yield of the orthosemidine. The ease with which paratoluenazophenetoil is resolved into its constituents is not determined by the presence of two substituents in the para-position to the azo-group, for paratoluenazoorthocresetoil, under the same conditions, behaves like benzeneazophenetoil, and gives a good yield of the orthosemidine. The benzyl ether of paratoluenazophenol, $C_6H_4Me \cdot N:N \cdot C_6H_4 \cdot O \cdot CH_2Ph$, like paratoluenazophenetoil, is also completely resolved into toluidine and the benzyl ether of paramidophenol.

Not only the position of the substituents, but also their nature, has a marked influence on the course of the reaction. When the para-position is occupied by an indifferent group, the semidine reaction takes place. When strongly electronegative or electropositive groups are present, diphenyl derivatives are obtained. Thus, parachlorohydrazobenzene yields a very small quantity of the orthosemidine, but no definite results could be obtained as to the nature of the main product of the reaction. Paraiodoazobenzene yields iododiamidodiphenyl, $NH_2 \cdot C_6H_3I \cdot C_6H_4 \cdot NH_2$. Paracetylamidohydrazobenzene yields a large quantity of paracetyldiamidodiphenylamine,



and, finally, paradimethylamidoazobenzene yields aniline, amidodimethylaniline, and the diphenyl derivative



E. C. R.

Action of Sodium Sulphide on Orthodiazophenol Chloride.
By A. PURGOTTI (*Gazzetta*, 22, ii, 614—620; compare Tassinari, *Abstr.*, 1892, 1316).—On slowly adding orthodiazophenol chloride

solution to sodium sulphide solution, considerable evolution of gas occurs; after heating on the water-bath and adding hydrochloric acid, a black, viscous mass separates, and is washed with dilute soda. By a somewhat lengthy process of purification, a *compound* is finally isolated which crystallises in long, silky needles melting at 127° , and has the constitution $S(S \cdot C_6H_4 \cdot OH)_2$ (?). It gives the normal molecular weight by the cryoscopic method in acetic acid solution, and is very soluble in alcohol, ether, acetic acid, chloroform, ethylic acetate, or acetone, sparingly so in benzene, and insoluble in water. It dissolves in alkalis with formation of metallic derivatives whose solutions give precipitates with silver, lead, mercury, copper, zinc, and cadmium salts. It gives orthohydroxyphenyl mercaptan on reduction with zinc and sulphuric acid, and, when treated with acetic anhydride, yields *orthodiacetoxytrithiobenzene*, $S(S \cdot C_6H_4 \cdot OAc)_2$, as a yellowish, viscous mass.

W. J. P.

Diazoamidobenzene and Paradiazoamidotoluene Benzoates and Metanitrobenzoates. By A. HALLER and A. GUYOT (*Compt. rend.*, 116, 353–355).—When an alcoholic solution of benzoic or metanitrobenzoic acid and aniline or toluidine is mixed with amylic nitrite, the following reactions take place:—(a) $Ph \cdot COO \cdot NH_3Ph + HNO_2 = Ph \cdot COO \cdot N_2Ph + 2H_2O$; (b) $Ph \cdot COO \cdot N_2Ph + Ph \cdot NH_2 = Ph \cdot COO \cdot NH_2Ph \cdot N_2Ph$. The same products are obtained when amylic nitrite is added in only half the quantity indicated by the equation.

Diazoamidobenzene benzoate, $Ph \cdot COO \cdot NH_2Ph \cdot N_2Ph$, crystallises from ether in yellow needles which alter rapidly if not quite free from nitrite, but are much more stable when pure, although they become brown after some time; they melt at 91° , and are soluble in almost all the ordinary solvents. *Diazoamidobenzene metanitrobenzoate* forms yellow crystals which melt at 90° and dissolve in all the usual solvents except light petroleum. *Paradiazoamidotoluene benzoate* crystallises from ether in long, yellow needles. *Paradiazoamidotoluene metanitrobenzoate* forms yellow needles which alter rapidly. When heated with dilute hydrochloric acid, it yields paratoluidine hydrochloride, metanitrobenzoic acid, and paracresol, which proves that these compounds are really diazoamido-derivatives.

Attempts to prepare the acetate, formate, and orthotoluate of diazoamidobenzene gave negative results, crystallised diazoamidobenzene being always formed. The action of amylic nitrite on a mixture of paratoluidine and ethylic cyanacetate or acetoacetate yields only diazoamidotoluene.

C. H. B.

Oxidation of Acid Hydrazides by Fehling's Solution. By H. STRACHE and S. IRITZER (*Monatsh.*, 14, 33–38).—It has been shown by Tafel, Gattermann, and others (*Abstr.*, 1892, 710, 843, 981) that when acid hydrazides are oxidised by means of copper acetate or ammoniacal copper solution they are converted into the corresponding derivatives of diphenylhydrazine. The authors find that if the hydrazides are treated with boiling Fehling's solution, the whole of the nitrogen is evolved in the free state. This is the case not only with the hydrazides of phenylhydrazine itself, but also with

those obtained from its homologues. Of the compounds examined, the only one hitherto unknown was the *hydrazide of stearic acid*, $C_{17}H_{35}CO \cdot NH \cdot NHPh$, which was prepared by heating the acid with an excess of phenylhydrazine to incipient boiling; it crystallises in white plates having an unctuous touch, and melts at $105-107^{\circ}$ (corr.).
H. G. C.

Action of Bromine on Dihydrobenzaldoxime. By A. EINHORN and F. K. DE NORWALL (*Ber.*, **26**, 623—625).—A *dibromo*-compound of the composition $C_7H_9Br_2NO$ is obtained when dihydrobenzaldoxime (compare Einhorn and Eichengrün, *Abstr.*, 1891, 65) is treated with a slight excess of bromine in well-cooled chloroform solution; it forms well-defined, forked crystals, melts at 122° , and decomposes with explosive violence at higher temperatures. It is decomposed by boiling hydrobromic acid with formation of benzaldehyde, and, although insoluble in alkalis and alkali carbonates, it is very readily decomposed by sodium carbonate in dilute alcoholic solution yielding carbonic anhydride, hydrogen bromide, and a very unstable compound, the nature of which was not ascertained; it liberates iodine from an alcoholic solution of potassium iodide. It would seem from these reactions that the bromo-derivative is a salt of the constitution represented by the formula $CH \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > C \cdot CH : NOBr, HBr$.

When β -benzaldoxime is treated with bromine in ice-cold chloroform solution, it is converted into β -benzaldoxime hydrobromide, the yield of which is, however, barely 50 per cent.
F. S. K.

Action of Benzenesulphonic Chloride on Amidoximes. By J. PINNOW (*Ber.*, **26**, 604—606; compare *Abstr.*, 1892, 461).—Phenylethenylamidoximebenzenesulphone is decomposed by boiling water yielding benzylcarbamide, benzenesulphonic acid, phenylethenylamidoxime, and ammonia, a fact which shows that the sulphone is an intermediate product in the conversion of phenylethenylamidoxime into benzylcarbamide, under the conditions previously stated (*loc. cit.*).

Ethenylamidoximebenzenesulphone, $NH_2 \cdot CMe : NO \cdot SO_2Ph$, prepared by treating ethenylamidoxime with benzenesulphonic chloride as previously described, melts at 130° , and is decomposed by boiling water yielding benzenesulphonic acid, acetic acid, and ammonia.

F. S. K.

Acid Salts and Constitution of Rosanilines. By A. ROSENSTIEHL (*Compt. rend.*, **116**, 194—197).—It is difficult to determine the exact constitution of the acid salts of the rosanilines when prepared from aqueous solutions, because the complete expulsion of the water is accompanied by a loss of acid. If, however, the dry colouring matter is subjected to the action of a current of dry hydrogen chloride or hydrogen bromide, mixed, if necessary, with air in order to moderate the reaction, absorption takes place with development of heat. If the products are allowed to remain in a vacuum over sulphuric acid for a few days, they acquire a constant weight. The poly-acid salts thus obtained have not the metallic lustre characteristic of

the original colouring matter; their aqueous solutions have the colour of the parent substance, but if the salts are exposed to moist air until they deliquesce, the colour of the liquid is then different. The poly-acid salts of rosaniline decompose spontaneously, but the methyl derivatives seem to be more stable.

The compounds analysed were rosaniline hydrochloride (C_{19}), rosaniline hydrobromide (C_{19}), hexamethylrosaniline hydrochloride, hexamethylrosaniline hydrobromide, tetramethyldiamidotriphenylcarbinol hydrochloride, and tetramethylamidotriphenylcarbinol hydrobromide. In the first four cases, the quantity of halogen present agreed closely with that calculated on the assumption that 4 atoms of the halogen are present in the molecule, and in the last two compounds, with the assumption that 3 atoms of the halogen are present in the molecule.

It follows that rosaniline and its congeners have both an alcoholic and a basic function with reference to acids, the former dominating, but being modified by the presence of the amido-groups. The compounds are intermediate between alkaline bases and alcohols. The colouring matters of the rosaniline group are ethereal salts formed from tertiary amido-alcohols of the benzene series. C. H. B.

Spectro-photometric Investigation of the Salts of Aromatic Bases. By A. WEIGLE (*Zeit. physikal. Chem.*, **11**, 227—247).—By means of photometric measurements, the author has examined the behaviour towards hydrochloric acid of some bases, which are either themselves colourless and form coloured salts, or are themselves coloured and form colourless salts. The first base examined was rosaniline. From the results, the amounts of mon-acid and tri-acid salts present in the solution were calculated, and it was then found that the sum of the two does not equal the total quantity of rosaniline present in each case. It must therefore be assumed that in these solutions there is, in addition to the above two coloured salts, a colourless compound, and it is highly probable that this compound is a di-acid salt of rosaniline. The nitranilines, nitrotoluidines, and three of the nitronaphthylamines were also examined. It was found that the salts which are most stable towards water are formed by those bases which contain the nitro- and amido-groups in the meta-position relatively to one another; the least stable salts are formed when these groups occupy the ortho-positions, and the para-compounds are intermediate in stability.] H. C.

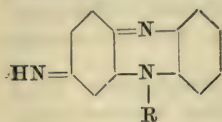
The Induline Group. By O. FISCHER and E. HEPP (*Annalen*, **272**, 306—354).—The authors propose that the indulines should now be systematically classed in four groups, in the following manner.

I. *Benzeneindulines*.—These compounds may be regarded as derivatives of phenazine, and their constitution may be represented by the general formula I (next page).

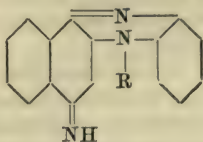
II. *Rosindulines*, or derivatives of $\alpha\beta$ -naphthaphenazine: the members of this class are of the general type represented by the formula II (next page).

III. *Isorosindulines*, or derivatives of the yet unknown $\alpha\beta$ -isonaph-

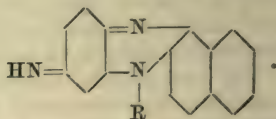
thaphenazine: these compounds may be represented by the general formula III.



I.

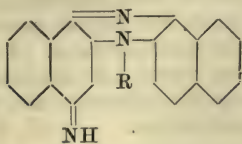
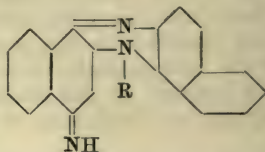
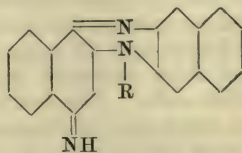


II.



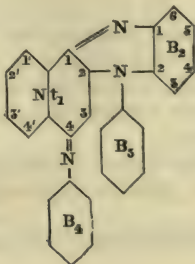
III.

IV. *Naphthindulines*, or derivatives of naphthazine: as there are, theoretically, five possible naphthazines, of which, however, only three can yield indulines, the members of this group would be represented by the following three types:—

Symmetrical $\alpha\beta$ -naphthinduline.Asymmetrical $\alpha\beta$ -naphthinduline. $\alpha\beta$ - $\beta\beta$ -naphthinduline.

According to this system of nomenclature, the isoparatolylrosinduline previously described (1890, 908) would be termed paramethylphenylrosinduline, isonaphthylrosinduline (*loc. cit.*) would be symmetrical $\alpha\beta$ -phenylnaphthinduline, and the so-called anilidoisonaphthylrosinduline (1891, 1044) would be symmetrical $\alpha\beta$ -anilidophenylnaphthinduline.

It is also proposed that, for the purpose of referring to the position of groups in the several nuclei, the benzene rings should be distinguished by the signs B_1 , B_2 , B_3 , &c., the nitrogen ring by the sign N_r ,



and the naphthalene ring by the sign Nt, that nucleus containing the quinoneimide group being invariably referred to as B₁ or Nt₁; in addition, the benzene and naphthalene carbon atoms are numbered, those in combination with the two nitrogen atoms being invariably numbered 1 and 2 respectively.

"Amidoazobenzeneinduline," C₁₈H₁₃N₃ (Abstr., 1890, 764; 1891, 1046), melts at 215°, not at 135° as previously stated; it is formed in small quantity, together with an induline of the composition C₂₄H₁₈N₄, paraphenylenediamine, diparadiamidophenylamine, and complex dyes which are insoluble in water, when amidoazobenzene hydrochloride is boiled with aniline hydrochloride in aqueous solution.

B₂-4-*Anilidoinduline*, NH:C₆H₃< $\begin{smallmatrix} \text{N} \\ \text{NPh} \end{smallmatrix}$ >C₆H₃NHPh, is formed, together with a compound which has probably the composition C₃₀H₂₃N₅, when diphenylmetaphenylenediamine is treated with nitrosoaniline and concentrated hydrochloric acid in alcoholic solution; it forms well-defined crystals melting at 246°, and having a bronze lustre. It dissolves in concentrated sulphuric acid yielding a bluish-green solution, which turns blue and then violet on adding water. The *nitrate*, C₂₄H₁₈N₄.HNO₃, is a crystalline compound, soluble in hot water, with a reddish-violet coloration.

B₄-2-*Methylphenylrosinduline*, C₂₉H₂₁N₃, can be obtained by heating phenylrosinduline (Abstr., 1890, 908) with orthotoluidine; it crystallises in prisms or needles, having a bronze lustre, melts at 197°, and is decomposed into rosindone and orthotoluidine when heated at 170° with hydrochloric acid and acetic acid.

B₂-4-*Amidophenylrosinduline*, C₂₈H₂₀N₄, is formed when a mixture of Illinsky's nitroso-β-naphthylamine, aniline, and paraphenylenediamine hydrochloride is heated slowly to 150°, and kept at this temperature for one to two hours; it crystallises in lustrous, greenish-bronze-coloured plates, melts at 147° with decomposition, and dissolves in concentrated sulphuric acid, yielding a green solution which becomes reddish-violet on diluting; its salts are comparatively readily soluble in hot water. The constitution of this induline is proved by the facts that it is formed when anilidonaphthaquinoneanil is substituted for the nitroso-β-naphthylamine in the above-mentioned mixture, and that its diazo-derivative is converted into phenylrosinduline on treatment with boiling alcohol.

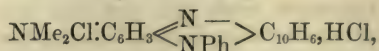
A *hydroxyrosinduline* of the composition C₂₂H₁₅N₃O is obtained when the amidophenylrosinduline just described is heated with glacial acetic acid and concentrated hydrochloric acid at 190–200° for about eight hours; it crystallises in greenish, lustrous prisms, melts at about 270° with decomposition, and dissolves in alcohol, yielding an eosin-coloured solution, which shows a yellowish-red fluorescence; its solution in concentrated sulphuric acid is dirty green, but on adding water it turns brown, a red, flocculent substance being afterwards precipitated.

A *hydroxyrosindone* of the composition C₂₃H₁₄N₂O₂ is formed when amidophenylrosinduline or the hydroxyrosinduline just described is heated with hydrochloric acid and glacial acetic acid at 220–225° for 15–20 hours; it forms reddish-brown crystals, having a green lustre;

its solution in concentrated sulphuric acid is green, that in alkalis rose-red, and its alcoholic solution shows a brownish-green fluorescence.

The isorosindulines are most conveniently prepared by treating a nitroso-base, such as nitrosoaniline or nitrosodimethylaniline, with α -naphthylamine or with 2 : 2'-diphenylnaphthylenediamine in aniline solution.

B₁-Dimethylisorosinduline hydrochloride,



can be obtained by heating nitrosodimethylaniline with aniline and α -naphthylamine hydrochloride, and subsequently converting the base into its hydrochloride. On treating the salt with soda, extracting with benzene, and evaporating the extract in absence of air, an *anhydride* of the base, having the composition $(\text{C}_{24}\text{H}_{20}\text{N}_3)_2\text{O}$, is deposited in almost black plates, which transmit red light; this compound decomposes at about 270° , rapidly absorbs carbonic anhydride from the air, and dissolves in concentrated sulphuric acid, yielding a green solution which changes, first, to dirty brown and then to reddish-violet on adding water. The *nitrate*, $\text{C}_{24}\text{H}_{19}\text{N}_3 \cdot 2\text{HNO}_3$, crystallises in beautiful, green plates.

Nt₂-2'-Anilido- $\alpha\beta$ -isorosinduline, $\text{C}_{28}\text{H}_{20}\text{N}_4$, is formed when 2 : 2'-diphenylnaphthylenediamine is warmed with nitrosoaniline and concentrated hydrochloric acid in alcoholic solution, and the hydrochloride thus produced decomposed with soda; it forms lustrous, bronze-coloured crystals, melts at a very high temperature, and dissolves in concentrated sulphuric acid, giving a yellowish-brown solution which, passing through green, becomes violet on diluting. The *hydrochloride*, $\text{C}_{28}\text{H}_{20}\text{N}_4 \cdot 2\text{HCl}$, dissolves in alcohol with a violet, and in chloroform with a blue, coloration; the *platinochloride*, $\text{C}_{28}\text{H}_{20}\text{N}_4 \cdot \text{H}_2\text{PtCl}_6$, is a dark blue, crystalline compound.

Nt₂-2'-Anilidophenyl- $\alpha\beta$ -isorosinduline, $\text{C}_{34}\text{H}_{24}\text{N}_4$, prepared from parannitrosodiphenylamine, dissolves in chloroform with a blue, and in concentrated sulphuric acid with a dirty violet, coloration. The *hydrochloride*, $\text{C}_{34}\text{H}_{24}\text{N}_4 \cdot \text{HCl}$, separates from alcohol in crystals; the *platinochloride*, $(\text{C}_{34}\text{H}_{24}\text{N}_4)_2 \cdot \text{H}_2\text{PtCl}_6$, forms lustrous, bronze-coloured crystals, and dissolves in alcohol with a blue coloration.

Nt₂-2'-Hydroxyisorosindone, $\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_2$, is formed when the preceding compound is heated with concentrated hydrochloric acid at 180° ; it forms small, bronze-coloured, lustrous crystals, and dissolves in soda with a deep blue, in ammonia and concentrated sulphuric acid with a violet, coloration; its alcoholic solution is red, and shows a green fluorescence.

An *induline ammonium base* of the composition $\text{C}_{30}\text{H}_{24}\text{N}_4\text{O}$, is obtained when nitrosodimethylaniline is heated with diphenylnaphthylenediamine and concentrated hydrochloric acid in alcoholic solution and the product decomposed with soda; it separates from alcohol in lustrous, bronze-coloured crystals, and dissolves in concentrated sulphuric acid, yielding a green solution, which passes through reddish-violet and becomes blue on the addition of water. The *hydrochloride*, $\text{C}_{30}\text{H}_{22}\text{N}_4 \cdot 2\text{HCl}$, separates from alcohol in crystals, and is moderately easily soluble in water.

Three naphthindulines, namely, symmetrical $\alpha\beta$ -phenylnaphthinduline (see above), symmetrical $\alpha\beta$ -anilidophenylnaphthinduline (naphthyl blue), and symmetrical Nt_2 -4-anilidonaphthinduline (naphthyl violet), are formed when benzeneazo- α -naphthylamine hydrochloride (1 part) is heated with α -naphthylamine hydrochloride (1 part) and aniline (10 parts); when, however, the proportion of α -naphthylamine hydrochloride is diminished, symmetrical $\alpha\beta$ -naphthinduline and other dyes are also obtained.

$\alpha\beta$ -Naphthinduline, $\text{C}_{26}\text{H}_{17}\text{N}_3$, is a black, crystalline substance with a green lustre; it melts at $248\text{--}250^\circ$, and is insoluble in water: it dissolves in concentrated sulphuric acid, yielding a blue solution, which, on diluting with water, first becomes violet, then dirty green, and finally red. Its solutions in acetic acid and in dilute hydrochloric acid have a magenta colour, and the alcoholic and acetic acid solutions of its salts are characterised by their fiery red fluorescence. The sulphate crystallises in brownish-red, moss-like needles. When the base is heated with a mixture of glacial acetic acid and concentrated hydrochloric acid at 200° , it yields oxynaphthindone (oxyphenyldinaphthazine), identical with the compound melting at 295° , previously described (Abstr., 1890, 910).

Numerous naphthindulines are formed by the interaction of nitroso- β -naphthylamine, aniline, and α -naphthylamine, the character of the product depending on the conditions of the experiment; when the nitroso-compound (1 part) is heated with α -naphthylamine hydrochloride (2 parts) and aniline (10 parts) at 100° , naphthyl violet and naphthyl blue appear to be the only dyes formed.

Symmetrical $\alpha\beta$ - Nt_2 -4-anilidonaphthinduline (naphthyl violet); $\text{C}_{32}\text{H}_{22}\text{N}_4$, prepared by either of the methods mentioned above, crystallises in brown plates, having a bronze lustre, and melting at a very high temperature; it dissolves in alcohol, benzene, ether, and chloroform with a reddish-violet, in glacial acetic acid with a bluish-violet, coloration, and its salts, although very sparingly soluble in water, are readily soluble in alcohol, yielding bluish-violet dichroic solutions, which transmit red, and reflect blue, light. It dissolves in concentrated sulphuric acid with a green coloration, but, on adding water to the solution, a blue, flocculent precipitate is produced; although solutions of its salts show only a feeble, brownish-red fluorescence, silk dyed with the solutions is highly fluorescent. The sulphonic acid is employed commercially and known as naphthyl violet. When the base is heated with glacial acetic acid at 200° , it is converted into an anilidonaphthindone of the composition $\text{C}_{32}\text{H}_{21}\text{N}_3\text{O}$; this compound crystallises in very dark, blue plates, which appear violet by transmitted light, and its solution in concentrated sulphuric acid is blue; it dissolves in alcohol with a reddish-violet coloration and a brownish-red fluorescence, but, on adding a mineral acid and diluting largely, the fluorescence changes to a bluish-green, the colour of the solution remaining unchanged. Nt_2 -4-Anilidonaphthinduline is decomposed by a mixture of glacial acetic acid and concentrated hydrochloric acid at 200° , yielding Nt_2 -4-oxynaphthindone, $\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}$, identical with the compound previously obtained from symmetrical $\alpha\beta$ -anilidophenylnaphthinduline (Abstr., 1891, 1044); this naphth-

indone crystallises in rectangular plates, and decomposes at about 300° .

Symmetrical $\alpha\beta$ -anilidophenylnaphthinduline (naphthyl blue) is a phenyl derivative of naphthyl violet, the anilido-group probably occupying the Nt_2 -4-position in both cases; its constitution is determined by the study of its products of decomposition with acids (Abstr., 1891, 1044) and by the fact that it can be formed by the condensation of benzeneazophenyl- α -naphthylamine (compare D.R.P. 63181). When the hydrochloride of the last-named compound is dissolved in phenol and the solution heated at 120 — 150° , ammonium chloride separates, and the solution turns violet; after treating with dilute soda to remove the phenol, and extracting the blue precipitate with alcohol and hydrochloric acid, the hydrochloride of symmetrical $\alpha\beta$ -anilidophenylnaphthinduline remains in lustrous needles. The alkali salt of the sulphonic acid of this naphthinduline is a dark-brown, lustrous powder, and constitutes the naphthyl blue of commerce.

$\alpha\beta$ -Anilidonaphthindone, $C_{32}H_{21}N_3O$, is formed, with separation of aniline, when $\alpha\beta$ -anilidophenylnaphthinduline is heated with 50 per cent. acetic acid at 250° ; it crystallises in bluish-black, lustrous plates, which appear violet by transmitted light, and dissolves in alcohol with a reddish-violet coloration, the solution showing a brownish-red fluorescence; it dissolves in concentrated sulphuric acid, yielding a blue solution, in which a red, flocculent precipitate is produced on the addition of water.

When the $\alpha\beta$ -oxynaphthindone, obtained by decomposing $\alpha\beta$ -anilidophenylnaphthinduline with a mixture of concentrated hydrochloric acid and glacial acetic acid, is heated with acetic anhydride and sodium acetate, it is converted into an *acetyl* derivative of the composition $C_{28}H_{18}N_2O_3$; this compound crystallises in slender, red, lustrous needles, melts at 290 — 295° , and dissolves in concentrated sulphuric acid with a reddish-violet coloration. The corresponding *benzoyl* derivative, $C_{33}H_{22}N_2O_3$, forms reddish-brown, lustrous crystals, and dissolves in concentrated sulphuric acid with a greenish-blue coloration. The *ethyl* derivative, $C_{28}H_{20}N_2O_2$, crystallises in lustrous, red plates or needles, and dissolves in alcohol, yielding a blood-red solution, which becomes orange and acquires a green fluorescence when acidified. The *methyl* derivative, $C_{27}H_{18}N_2O_2$, forms lustrous plates, melts above 330° , and dissolves freely in alcohol with a cherry-red coloration. The *bromo*-derivative, $C_{26}H_{13}N_2O_2Br$, prepared by treating the oxynaphthindone with a chloroform solution of bromine, crystallises in lustrous, reddish plates.

In preparing $\alpha\beta$ -anilidophenylnaphthinduline from benzeneazo- α -naphthylamine, or from nitroso- β -naphthylamine, phenylrosinduline, anilidonaphthaquinonedianil (Abstr., 1891, 1044), and other substances are obtained as bye-products. Anilidonaphthaquinonedianil separates from a mixture of benzene and light petroleum in orange-yellow plates melting at 159° , and from alcohol in orange-red prisms, which melt at 142 — 143° and contain $\frac{1}{2}$ mol. C_2H_6O .

A substance, which appears to have the composition $C_{26}H_{17}N_3$, and which is, in all probability, an anilido-derivative of symmetrical $\alpha\beta$ -naphthazine, is formed when nitroso- β -naphthylamine is treated

with α -naphthylamine hydrochloride and aniline under particular conditions; it crystallises in yellowish-brown needles, having a greenish lustre, melts at 280° , and its solutions in alcohol and benzene show a green fluorescence; it dissolves in glacial acetic acid with a bluish-violet coloration. When this anilidonaphthazine is heated with glacial acetic acid and concentrated hydrochloric acid at 200° , it is decomposed into aniline and an *oxynaphthazine* of the composition $C_{20}H_{12}N_2O$; the latter crystallises in dark red needles, dissolves in concentrated sulphuric acid with a blue coloration, and forms a *hydrochloride* which crystallises in dark red needles having a green reflex; on distillation with zinc-dust, it yields symmetrical naphthazine.

When α -nitroso- β -naphthol is heated with α -naphthylamine hydrochloride and α -naphthylamine in alcoholic solution, hardly a trace of a naphthinduline is formed; if, after boiling for 6—7 hours, the solution be kept for a long time, a compound of the composition $C_{30}H_{20}N_2O$ is deposited in brown crystals. This substance melts at 237° , and dissolves in concentrated sulphuric acid, yielding a green solution, which turns blue on adding a little water, but becomes violet on diluting largely, a bronze-coloured powder being finally precipitated; it is probably a *naphthalidonaphthaquinonenaphthalide* of the constitution $C_6H_4 \cdot C(N \cdot C_{10}H_7) \cdot CO \cdot C(NH \cdot C_{10}H_7) \geq CH$. The mother liquors from this product yield, on evaporation, a compound of the composition $C_{40}H_{27}N_3O$, which is probably a *dinaphthalidonaphthaquinoneanilide*; it crystallises in brownish-red plates, melts at 212° , and dissolves in concentrated sulphuric acid with a blue coloration, the solution becoming violet, then dirty red, and a red, flocculent substance separating, on the addition of water.

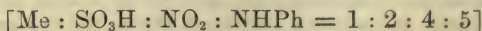
F. S. K.

Isoparatolylrosinduline. By C. SCHRAUBE and E. ROMIG (*Ber.*, 26, 575—582).—Having obtained an induline (azocarmine) by heating benzeneazo- α -naphthylamine hydrochloride with aniline and aniline hydrochloride (D.R.P., No. 45370), the authors attempted to prepare a homologue by similarly treating benzeneazoparatolyl- α -naphthylamine, but found that an induline, identical with that previously obtained, was produced. Fischer and Hepp having subsequently described an isoparatolylrosinduline, which they prepared by heating benzeneazoparatolyl- α -naphthylamine with aniline and alcohol (*Abstr.*, 1890, 908), the authors have made a fresh investigation of the subject, in order to explain the difference in the results of the two series of experiments. They have synthesised isoparatolylrosinduline in the manner described below, and find that it has properties quite different from those assigned to it by Fischer and Hepp; the substance described by the latter was, without doubt, simply impure phenylrosinduline.

Chloronitrotoluenesulphonic acid [$Me : SO_3H : NO_2 : Cl = 1 : 2 : 4 : 5$] is obtained when metachlorotoluene is dissolved in ice-cold anhydrosulphuric acid, the solution warmed at 50° until a portion gives no precipitate on adding water, and, after cooling, treated with a mixture of concentrated sulphuric and nitric acids at 20 — 25° ; it was isolated in the form of its *barium* salt, which crystallises in yellowish-brown plates or needles containing 2 mols. H_2O . When the barium salt is

reduced with zinc-dust in boiling aqueous solution, the chloramido-toluenesulphonic acid obtained in this way, boiled with moderately dilute sulphuric acid, and the diluted solution treated with soda, *chloramidotoluene* is precipitated; this base forms a colourless, crystalline hydrochloride, and, since it yields only a diazoamido-derivative with paranitrodiazobenzene, and not an amidoazo-derivative, it must be a chloroparatoluidine.

The *aniline* salt of *nitrotolylphenylaminesulphonic acid*



is formed when the barium salt of chloronitrotoluenesulphonic acid is boiled with aniline hydrochloride in aqueous solution and the sparingly soluble aniline chloronitrotoluenesulphonate, which is precipitated in long, yellow needles, heated with aniline at 160° for 2–3 hours; the salt crystallises in brownish-yellow needles, and is only sparingly soluble in water. The corresponding *sodium* salt crystallises in golden plates. The *barium* salt crystallises in yellow plates with 2 mols. H_2O .

Nitrotolylphenylamine $[\text{Me} : \text{NHPh} : \text{NO}_2 = 1 : 5 : 4]$ is produced when the barium salt just mentioned is treated with dilute sulphuric acid and the solution of the sulphonic acid heated with sulphuric acid at 145° ; it crystallises in yellowish-red, six-sided plates, and melts at 110° .

Phenylorthotolylenediamine, $\text{NHPh} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2$ $[\text{Me} : \text{NH}_2 : \text{NHPh} = 1 : 4 : 5]$, prepared by reducing the preceding compound with zinc-dust in ammoniacal alcoholic solution, crystallises in slender, colourless needles, and melts at $87\text{--}88^\circ$.

Isoparatolylrosinduline, $\text{C}_6\text{H}_3\text{Me} < \begin{smallmatrix} \text{N} = \text{C} \cdot \text{C}_6\text{H}_4 \\ | \\ \text{NPh} \cdot \text{C} : \text{CH} \end{smallmatrix} > \text{C} \cdot \text{NPh}$, is produced when phenylorthotolylenediamine (110 parts) and β -hydroxy- α -naphthaquinoneanil (130 parts) are boiled with a mixture of 37 per cent. hydrochloric acid (50 parts) and alcohol (1000 parts) until solution is complete and the deep-red colour ceases to become more intense; on adding ammonia to the hot solution, isoparatolylrosinduline is precipitated in slender, brownish-red needles melting at 224.5° . It separates from hot alcoholic benzene in dark-brown, lustrous crystals, which appear red by transmitted light; it dissolves in concentrated sulphuric acid with a green coloration.

F. S. K.

Acetalylphenylcarbamide. By P. FRITSCH (*Ber.*, **26**, 427–428).—This substance, $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$, is obtained by treating acetalamine with phenylic cyanate; it forms long needles with a silky lustre, and melts at 55° . When warmed with dilute sulphuric acid (1 : 2), it is converted into a substance $\text{CO} < \begin{smallmatrix} \text{NPh} \cdot \text{CH} \\ | \\ \text{NH} - \text{CH} \end{smallmatrix} >$, which forms a white, crumbly mass, melts above the boiling point of sulphuric acid, and, when treated with sodium methoxide and methylic iodide, yields a *methyl derivative* which melts at 216° , and forms small, silky crystals.

C. F. B.

Constitution of Thiocarbamide and Phenylthiobiuret. By A. CLAUS (*J. pr. Chem.* [2], **47**, 135—138).—A discussion of the subject designed to show that it is incorrect to argue that a sulphur compound is a thioalcohol or thiophenol, because it is convertible into a thio-ether by the action of an alkyl haloid and an alkali. This has a special bearing on Fromm's interpretation of the reactions of phenylthiobiuret (Abstr., 1892, 844), which, in the author's opinion, by no means prove the existence of two SH groups in that compound.

A. G. B.

Action of Diazobenzene Chloride on α -Hydroxyuvitic acid. By A. BLANK (*Ber.*, **26**, 602—604).—It is stated in a recent French patent (No. 221,370) that α -hydroxyuvitic acid reacts readily with diazo-compounds, yielding products in which the azo-group occupies the meta-position relatively to the hydroxy-radicle; such a result being contrary to all experience, the author has investigated the matter, and found the statement to be incorrect.

When an ice-cold solution of α -hydroxyuvitic acid in 15 per cent. sodium carbonate is treated with diazobenzene chloride, a yellow, crystalline sodium salt is formed. The acid obtained on decomposing this sodium salt with hydrochloric acid crystallises in lustrous, yellow plates, melts at 198—199° (uncorr.), and decomposes at a higher temperature with evolution of carbonic anhydride; it is identical with the compound obtained by the action of diazobenzene chloride on ortho-hydroxymetatoluic acid, so that it must be a benzeneazoorthohydroxymetatoluic acid of the constitution $\text{N}_2\text{Ph}\cdot\text{C}_6\text{H}_2\text{Me}(\text{OH})\cdot\text{COOH}$ [$\text{N}_2\text{Ph} : \text{Me} : \text{OH} : \text{COOH} = 1 : 3 : 4 : 5$].

F. S. K.

Dihydrobenzaldehyde. By A. EINHORN (*Ber.*, **26**, 451—458).—In the light of the constitutional formula for anhydroecgonine, recently proposed by Einhorn and Tahara (this vol., i, 377), the author now considers that the dihydrobenzaldehyde obtained from this compound (Abstr., 1891, 65) is the Δ^4 -derivative, and the following experiments support this hypothesis.

Dihydrobenzamide, $\text{CH} \begin{smallmatrix} \text{CH}-\text{CH} \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix} \text{C}\cdot\text{CONH}_2$, is obtained by treating the dihydrobenzoic acid (*loc. cit.*) with phosphoric chloride, and pouring the solution into concentrated aqueous ammonia. It crystallises from ether in white needles, and melts at 105°.

When a 12 per cent. solution of bromine in chloroform is added to one of dihydrobenzoic acid in the same solvent, a *dibromo*-additive product is formed; it crystallises from alcohol in white, prismatic tables, and melts at 166°. A *tetrabromide* is obtained when the dihydrobenzoic acid is dissolved in glacial acetic acid and heated with bromine in a sealed tube at 100°; it crystallises from benzene in nodular groups of crystals, and melts at 183°. On heating the dihydrobenzoic acid with sodium amalgam and water, it is converted into Δ^1 -tetrahydrobenzoic acid (Aschan, this vol., i, 34).

A. R. L.

α -Phenylcinnamic acid. By R. MÜLLER (*Ber.*, **26**, 659—665).— α -Phenylcinnamic acid is purified by crystallisation from light petr-

oleum, and melts at 172° , instead of 169 — 170° as stated by Oglialoro; attempts to isolate a second modification by fractional crystallisation of the sodium and barium salts were unsuccessful. The acid does not combine directly with bromine, but yields an additive compound by the action of hydrogen bromide at 125° ; this is deposited from alcohol in needles, melts at 185° , and on treatment with alcoholic potash yields stilbene.

Methylic α -phenyldibromocinnamate, which melts at 111° instead of 106 — 108° , as stated by Cabella, gives *methylic α -phenyl- β -bromocinnamate* by the action of alcoholic potash; this crystallises from dilute alcohol in groups of colourless needles, melts at 70° , and on hydrolysis yields α -phenyleinnamic acid; on reduction of the bromosalt in acid solution, methylic phenyleinnamate is regenerated.

Bromostilbene is formed in small quantity in the preparation of methylic α -phenyl- β -bromocinnamate, and is readily obtained by the action of bromine on sodium α -phenyleinnamate in molecular proportion in aqueous solution at 40 — 45° ; it crystallises in prisms, and melts at 22 — 25° .
J. B. T.

Phenyl- α -hydroxycrotonic acid. By G. PULVERMACHER (*Ber.*, 26, 462—464).—The compound, melting at 98° , which Biedermann obtained from phenyl- α -hydroxycrotonic acid and phenylhydrazine (*Abstr.*, 1892, 473), has probably the constitution $\text{NPh} < \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} > \text{CH} \cdot \text{CH} \cdot \text{CPh}$. When it is boiled with hydriodic acid and phosphorus, it yields phenyl- α -hydroxycrotonic acid, ammonia, and aniline. A certain amount of phenylhydrazine is obtained when the compound is boiled with alkalis, or fuming hydrochloric acid; also when it is treated with cold fuming hydrobromic acid. γ -Phenylbutyric acid is formed by heating the compound with hydriodic acid and phosphorus at 160° in a sealed tube.
A. R. L.

Bergapten. By C. POMERANZ (*Monatsh.*, 14, 28—32; compare *Abstr.*, 1892, 71).—In continuation of his investigation of this substance, the author has obtained *nitrobergapten*, $\text{C}_{12}\text{H}_7(\text{NO}_2)\text{O}_4$, by the action of nitric acid on bergapten moistened with acetic acid; it crystallises from the latter in pale yellow needles, becomes brown at 230° , and melts at 256° with decomposition. When triturated with a little acetic acid, and allowed to remain for an hour with 20 times its weight of fuming nitric acid, it yields a product which, in addition to unaltered nitrobergapten, contains *nitromethoxycumaronecarboxylic acid*, $\text{CH} < \begin{smallmatrix} \text{CH} \\ \text{O} \end{smallmatrix} > \text{C}_6(\text{OH})(\text{OMe})(\text{NO}_2) \cdot \text{COOH}$, and the corresponding *aldehyde*. The former crystallises in pale yellow, prismatic needles, and melts at 200° with decomposition, and the latter forms small, yellowish-red crystals, which darken at 200° , and decompose at a higher temperature. These results are in full agreement with the views already expressed as to the constitution of bergapten, and the author is now endeavouring to ascertain the exact orientation of the different groups in the benzene nucleus.
H. G. C.

Chestnut Bark Tannin. By H. TRIMBLE (*Chem. News*, 67, 7, 8).—With the object of comparing the tannin from chestnut bark with that from the wood, material was taken from a tree 30 years old, cut in August, and from which the bark was immediately removed, air-dried, and powdered. The total tannin was found to be 7.31 per cent., the wood yielding 7.85 per cent.; the bark also contained resin 1.09, mucilage 3.06, glucose 1.35, moisture 10.0, ash 4.71, and cellulose 45.44 per cent. The tannin, as extracted from the bark by commercial ether, was darker than that from the wood; but nevertheless, after systematic purification, in a manner somewhat similar to that already described (Abstr., 1892, 716), it proved to be identical with the chestnut wood tannin.

D. A. L.

Derivatives of Gallic acid. By A. BIÉTRIX (*Bull. Soc. Chim.* [3], 7, 623—625).—*Ethylic dibromogallate*, $C_6Br_2(OH)_3\cdot COOEt$, obtained by treating ethylic gallate with an excess of bromine, crystallises from water in delicate, translucent needles, and melts at 137°.

Methylic gallate, $C_6H_2(OH)_3\cdot COOMe$, is prepared by saturating a solution of gallic acid in methyl alcohol with hydrogen chloride; it crystallises from water in transparent needles containing 3 mols. H_2O , melts at 112°, and gives a blackish-green coloration with ferric chloride. The *dibromo*-derivative forms silky needles, and melts at 139°.

A. R. L.

Parethoxyorthotoluenesulphonic acid and its Derivatives. By P. J. DASHIELL (*Amer. Chem. J.*, 15, 126—129).—In this paper *barium parethoxyorthotoluenesulphonate*, with 4 mols. H_2O , and the *lead*, with 3 mols. H_2O , *calcium*, with 3 mols. H_2O , *magnesium*, with 6 mols. H_2O , *zinc*, with 6 mols. H_2O , *copper*, with 6 mols. H_2O , *silver*, *potassium*, with 1 mol. H_2O , *sodium*, and *ammonium* salts are described. They were obtained from the acid prepared by the decomposition of *paradiazotolueneorthosulphonic acid* by alcohol (this vol., i, 325). The *sulphonic chloride* is a light brown, mobile oil.

A. G. B.

Ethereal Sulphinates. By R. OTTO and A. RÖSSING (*J. pr. Chem.* [2], 47, 152—152).—Methylic β -naphthalenesulphinate has been already described (Abstr., 1892, 623). The compound which is simultaneously produced during the preparation is β -naphthyl disulphoxide (m. p. 107°), not methylnaphthylsulphone formate, as previously suggested (*loc. cit.*). The sulphinate is easily oxidised to methylic β -naphthylsulphonate, which melts at 55—56° (Krafft and Roos, Abstr., 1892, 1219).

Methylic α -naphthalenesulphinate is prepared similarly to the β -derivative. It is a yellowish oil, has a slight odour, and dissolves easily in ether or alcohol, but only sparingly in boiling light petroleum. It is easily hydrolysed by potash, and is thus distinguished from its isomeride, methylic- α -naphthylsulphone (m. p. 102—103°). It is easily oxidised to methylic α -naphthylsulphonate, which melts at 78°, not 75° (Krafft and Roos, *loc. cit.*). Some α -naphthylsulphoxide is produced during the preparation of the sulphinate, and is separated by light petroleum, in which it is insoluble.

Ethyllic β -naphthalenesulphinate, prepared from sodium β -naphthalenesulphinate and ethylic chlorocarbonate, is an aromatic, yellowish oil, insoluble in water, easily soluble in alcohol and ether, but only sparingly in light petroleum; it is readily hydrolysed by potash, and oxidised by potassium permanganate to the corresponding sulphonate.

Methylic benzenesulphinate, prepared from sodium benzenesulphinate and methylic chlorocarbonate, is a mobile oil, insoluble in water, but soluble in alcohol and ether. Hot water decomposes it into methyl alcohol and benzenesulphinic acid, which becomes converted into benzene disulphoxide and benzenesulphonic acid.

Methylic paratoluenesulphinate is a yellow oil which is very unstable in air. Oxidation converts it into the corresponding sulphonate, which melts at about 30° . With water, it behaves like the benzenesulphinate.

Methylic parabromobenzenesulphinate, from sodium parabromobenzenesulphinate (prepared from parabromobenzenesulphonic chloride and zinc-dust in alcohol) and methylic chlorocarbonate in methyl alcohol, is a yellowish oil, insoluble in water, but soluble in ether and alcohol.

Experiments with sulphinates other than those of the alkali metals showed that the reaction with alkyl chlorocarbonates always yields alkylic sulphinates. It was also proved that both zinc and silver sulphinates give sulphones when treated with alkylic haloids, showing that there is no difference between their behaviour and that of the alkali sulphinates in this respect (Abstr., 1880, 810). Attempts to convert ethylic benzenesulphinate into its isomeric sulphone proved futile.

A. G. B.

Chemical Behaviour of Ethereal Salts of Sulphinic acids.

By R. OTTO and G. ZUSCHLAG (*Ber.*, 26, 430—435).—A continuation of Otto and Rössing's experiments (preceding abstract). When a current of dry hydrogen sulphide is passed through ethylic benzenesulphinate heated at 110° , ethyl alcohol distils over, and when this ceases, the residue consists of phenylic benzenethiosulphonate; if, however, the current of gas be continued for a longer period, the residue consists of sulphur and a mixture of sulphur compounds similar to that obtained by Otto (*J. pr. Chem.* [2], 37, 207) by the action of hydrogen sulphide on alcoholic solutions of benzenesulphinic acid. Ethylenediphenylsulphone undergoes no change when treated with hydrogen sulphide. When ethylic benzenesulphinate is shaken with an excess of a concentrated, colourless, aqueous solution of potassium sulphide, heat is developed. The oily portion of the product consists of a mixture of phenylic bisulphide (m. p. 60°) and liquids containing more sulphur, whilst the aqueous liquid contains alcohol and potassium benzenethiosulphonate; it yields, on treatment with carbonic anhydride, an oil. When the latter is distilled in a current of steam, thiophenyl passes over, and a mixture of sulphur, phenyl bisulphide, and higher sulphur derivatives remains.

A. R. L.

Conversion of Pentene Derivatives into Indene Derivatives.

By T. ZINCKE and H. GÜNTHER (*Annalen*, 272, 243—270).—Hexa-

chloroketoindene, $C_6Cl_4 \langle \begin{smallmatrix} CO \\ CCl \end{smallmatrix} \rangle CCl$, is formed when either of the hexachlorhydroxypentenecarboxylic acids previously described (Abstr., 1890, 754) is heated with 8—10 parts of water: the acid dissolves at first, but the solution quickly becomes turbid, carbonic anhydride is evolved, and the product is precipitated in a flocculent condition. The decomposition of the acid takes place in accordance with the equation $2C_6Cl_6H_2O_3 + H_2O = C_9Cl_6O + 6HCl + 3CO_2$, the yield of hexachloroketoindene being almost theoretical; attempts to isolate some intermediate product in order to throw light on this remarkable reaction were unsuccessful.

Hexachloroketoindene crystallises in golden plates, melts at 148—149°, and separates unchanged from nitric acid of sp. gr. 1.4; molecular weight determinations by the boiling point method confirm the molecular formula C_9Cl_6O . Its *oxime* melts at 255° with decomposition.

Pentachlor- α -anilido- α -ketoindene, $C_6Cl_4 \langle \begin{smallmatrix} CO \\ C(NHPh) \end{smallmatrix} \rangle CCl$, prepared by heating the preceding compound with aniline in alcoholic solution, crystallises in lustrous, dark red needles, and melts at 236—237°; it is very stable towards alkalis, but is readily decomposed by acids. The corresponding *paratoluido-derivative*, $C_9Cl_5O \cdot NH \cdot C_6H_7$, obtained in like manner, melts at 243°.

Pentachlor- α -hydroxy- α -ketoindene, $C_6H_4 \langle \begin{smallmatrix} CO \\ C(OH) \end{smallmatrix} \rangle CCl$, is formed when hexachloroketoindene is heated with alkalis, and also when the anilido-derivative just described is warmed with concentrated sulphuric acid for several hours. It is an orange, crystalline powder, melts at 177°, decomposes carbonates and alkali acetates, and readily changes into an insoluble, probably polymeric, modification; it separates from acetic acid in orange-red, and from benzene in colourless, crystals, which contain the solvent and are unstable. The *hydrate*, $C_9HCl_5O_2 + H_2O$, is obtained as a salmon-coloured precipitate on decomposing the sodium derivative with hydrochloric acid; it turns orange and begins to lose water at about 111° and melts at 174—177°. The *sodium* derivative crystallises in red needles, and seems to have the composition $C_9H_4Cl_5O_3Na$. A red, crystalline substance of the composition $C_{15}Cl_5H_8NO_2$ is formed when the hydroxy-compound is treated with aniline in glacial acetic acid solution; it melts at 205° and is readily decomposed by mineral acids. The *methoxide*, $C_{10}H_5Cl_5O_3$, prepared by boiling the hydroxy-compound or its hydrate, with methyl alcohol, crystallises in long, reddish-yellow needles, begins to lose methyl alcohol at 110°, and has no definite melting point; the corresponding *ethoxide* crystallises in yellow needles and is less stable. The *acetyl* derivative, $C_{11}H_3Cl_5O_3$, crystallises in lustrous, golden needles or plates, and melts at 178—179°.

Hexachlor- α -diketohydrindene, $C_6Cl_4 \langle \begin{smallmatrix} CO \\ CO \end{smallmatrix} \rangle CCl_2$, prepared by treating pentachlorhydroxyketoindene with chlorine in glacial acetic acid solution, crystallises in short prisms, and melts at 155—156°.

Hexachloracetophenoneorthocarboxylic acid, $CHCl_2 \cdot CO \cdot C_6Cl_4 \cdot COOH$,

is formed when the diketone just described is treated with concentrated alcoholic potash in the cold; it crystallises in colourless needles, melts at 192—193°, previously softening, and forms a colourless, crystalline, insoluble silver salt.

Heptachloracetphenoneorthocarboxylic acid, $\text{CCl}_3 \cdot \text{CO} \cdot \text{C}_6\text{Cl}_4 \cdot \text{COOH}$, is deposited when the preceding compound is dissolved in excess of sodium carbonate, and chlorine passed into the solution; it is a colourless, crystalline substance, melts at 240—241°, and is decomposed by soda into chloroform and tetrachlorophthalic acid.

Octochlor- α -ketohydrindene, $\text{C}_6\text{Cl}_4 \langle \text{CO} \rangle \text{CCl}_2$, is best prepared by heating hexachloroketoindene with manganese dioxide and hydrochloric acid at 180°; it forms colourless nodules, melts at 112—113°, and is reconverted into hexachloroketoindene on treatment with stannous chloride.

Hexachlorodibrom- α -ketohydrindene, $\text{C}_6\text{Cl}_4 \langle \text{CO} \rangle \text{CClBr}$, obtained by treating the hexachloro-compound with bromine, is an almost colourless, crystalline, granular substance, and melts at 105—106° with elimination of bromine, being reconverted into the hexachloro-compound.

Octochlororthovinylbenzoic acid, $\text{CCl}_2 \cdot \text{CCl} \cdot \text{C}_6\text{Cl}_4 \cdot \text{COOH}$, is produced when octochloroketohydrindene is treated with alcoholic soda; it crystallises in lustrous, colourless needles, and melts at 158—159°; its *methylic* salt, $\text{C}_{10}\text{H}_3\text{Cl}_7\text{O}_2$, is a colourless, crystalline substance melting at 77—78°.

Octochlorindene, $\text{C}_6\text{Cl}_4 \langle \text{CCl}_2 \rangle \text{CCl}$, prepared by treating hexachloroketoindene with phosphorus pentachloride at 190—200°, crystallises in colourless needles, and melts at 85°. F. S. K.

Derivatives of Phthalazine and Isoindole. By S. GABRIEL and A. NEUMANN (*Ber.*, 26, 521—527 and 705—713).—Phthalazone,

$\text{C}_6\text{H}_4 \langle \text{CH} \rangle \text{N}_2\text{H}$, is obtained by heating the product of the action of bromine on phthalide with water, neutralising the mixture of hydrobromic and phthaldehydic acids thus obtained with soda and then adding hydrazine sulphate to the hot solution. It crystallises in long, lustrous needles, melts at 182°, boils at 337° under 755 mm. pressure, and dissolves in alkalis and mineral acids. When reduced with zinc and hydrochloric acid, it is converted into phthalimidine.

3-Methylphthalazone, $\text{C}_6\text{H}_4 \langle \text{CH} \rangle \text{N}_2\text{Me}$, is obtained by heating an alcoholic solution of phthalazone with soda and methylic iodide. It distils as a yellow oil at 301° under 755 mm. pressure, crystallises from acetic acid in forms resembling calc-spar, melts at 102—103°, and has basic properties.

4-Chlorophthalazine, $\text{C}_6\text{H}_4 \langle \text{CH} \rangle \text{N}_2$, is obtained by heating phthalazone with phosphorus oxychloride. It crystallises in yellow needles, melts at 113°, and dissolves easily in dilute acids. The solution of

the hydrochloride yields with gold chloride sparingly soluble, yellow needles, with potassium dichromate orange-yellow tablets, with picric acid slender needles, and with potassium ferrocyanide a brownish-yellow, crystalline powder. The *platinochloride*, $(C_8H_5N_2Cl)_2 \cdot H_2PtCl_6$, is sparingly soluble and crystallises in slender needles.

4-Methoxyphthalazine, $C_6H_4 < \begin{smallmatrix} \text{CH} \\ \text{C(OMe)} \end{smallmatrix} > N_2$, is obtained by boiling a methyl alcoholic solution of chlorophthalazine with sodium methoxide. It crystallises in yellow needles, melts at $60-61^\circ$, has a faint, fruity odour, and yields crystalline salts.

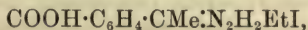
Dihydroisoindole, $C_6H_4 < \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} > NH$, obtained by reducing chlorophthalazine with zinc and hydrochloric acid, is an oil which boils at 213° under 762 mm. pressure, and has an odour resembling that of benzylamine; it has an alkaline reaction, and takes up carbonic anhydride on exposure to the air to form a crystalline mass. The *hydrochloride* darkens and melts at $255-256^\circ$. The *platinochloride*, $(C_8H_5N)_2 \cdot H_2PtCl_6$, crystallises in flat, orange-yellow needles. The *nitrosamine*, $C_8H_5N \cdot NO$, crystallises in long, slender needles, and melts at $96-97^\circ$.

1-Methylphthalazone, $C_6H_4 < \begin{smallmatrix} \text{CMe} \\ \text{CO-} \end{smallmatrix} > N_2H$, is obtained by adding a solution of hydrazine sulphate in sodium hydroxide to a solution of acetophenoneorthocarboxylic acid and heating the mixture for one hour on the water bath. It crystallises in short prisms, melts at 222° , boils at $347-348^\circ$ under 755 mm. pressure, and is soluble in alkalis and acids.

1-Methylphthalimidine, $C_6H_4 < \begin{smallmatrix} \text{CHMe} \\ \text{CO-} \end{smallmatrix} > NH$, or $C_6H_4 < \begin{smallmatrix} \text{CHMe} \\ \text{C(NH)} \end{smallmatrix} > O$, is obtained by reducing the preceding compound with zinc and hydrochloric acid. It distils at a very high temperature, crystallises in colourless, transparent rhombs, melts at $110-111^\circ$, is a feeble base, and yields a crystalline aurochloride and platinochloride.

1 : 3-Methylethylphthalazone, $C_6H_4 < \begin{smallmatrix} \text{CMe} \\ \text{CO-} \end{smallmatrix} > N_2Et$, is obtained by boiling an alcoholic solution of methylphthalazone with sodium hydroxide and ethylic iodide. It boils at 309° under 735 mm. pressure, melts at $75-76^\circ$, and is soluble in hydrochloric acid.

The *hydrazone ethiodide of acetophenonecarboxylic acid*,



is obtained as sodium salt in the preparation of the preceding compound. It crystallises in thick, colourless prisms, and melts at $188-189^\circ$ with formation of water, ethylic iodide, and 1-methylphthalazone. It is a strong acid, dissolving easily in ammonia and the fixed alkalis, and turns out carbonic anhydride from carbonates; it is precipitated from these solutions in a crystalline condition by strong acids.

The bye-product obtained in methylating phthalazine is very similar to the last compound, and is the *hydrazone methiodide of phthalaldehydic acid*, $COOH \cdot C_6H_4 \cdot CH : N_2H_2MeI$. It melts at $179-180^\circ$

with decomposition into phthalazone, and is precipitated from its salts by hydrochloric acid in lustrous rhombs or needles.

1 : 4-Methylchlorophthalazine, $C_6H_4 < \begin{smallmatrix} CMe \\ CCl \end{smallmatrix} > N_2$, obtained by the action of phosphorus oxychloride on 1-methylphthalazone, crystallises in long, lustrous needles, melts at 130° , has basic properties, and yields crystalline salts.

1 : 4-Methylethoxyphthalazine, $C_6H_4 < \begin{smallmatrix} CMe \\ C(OEt) \end{smallmatrix} > N_2$, is obtained by boiling the preceding compound with sodium ethoxide and alcohol. It crystallises in slender needles, melts at $56-57^\circ$ and is easily soluble in acids. The solution in hydrochloric acid gives crystalline precipitates with picric acid, potassium dichromate, platinic chloride, and potassium ferrocyanide.

Methylisoindole, $C_6H_4 < \begin{smallmatrix} CMe \\ CH_2 \end{smallmatrix} > N$ or $C_6H_4 < \begin{smallmatrix} CHMe \\ CH \end{smallmatrix} > N$, is obtained by reducing methylchlorophthalazine with hydriodic acid and phosphorus, or better with zinc and hydrochloric acid, when it is obtained as the zinc double salt, $(C_9H_9N)_2 \cdot H_2ZnCl_4$. The *platinochloride*, $(C_9H_9N)_2 \cdot H_2PtCl_6 \cdot H_2O$, crystallises in slender, yellow needles, does not lose its water of crystallisation at 100° , and decomposes at a higher temperature. The *picrate*, $C_9H_9N \cdot C_6H_3N_3O_7$, is obtained as a fine crystalline precipitate. The *free base* is a colourless oil with an odour resembling that of quinoline; it is volatile with steam and quickly turns yellow on exposure to air. A wood splinter remains uncoloured when placed in an acid solution of the base, but if alkali is added and the mixture boiled, a cherry-red coloration is produced.

1-Methyldihydroisoindole, $C_6H_4 < \begin{smallmatrix} CHMe \\ CH_2 \end{smallmatrix} > NH$, is obtained by the further reduction of methylchlorophthalazine with zinc and hydrochloric acid. It distils at 213° under 758 mm. pressure, has a strong alkaline reaction when dissolved in water, and absorbs carbonic anhydride. The *hydrochloride* crystallises in very slender needles, and melts at 170° with a violet coloration. The *nitrosamine* crystallises in lustrous spears, and melts at 98° .

1-Benzylphthalazone, $C_6H_4 < \begin{smallmatrix} C(CH_2Ph) \\ CO \end{smallmatrix} > N_2H$, is obtained by the action of hydrazine sulphate on an alkaline solution of desoxybenzoïn-carboxylic acid. It crystallises in long, colourless needles, and melts at 196° . When treated with phosphorus oxychloride, it yields 1 : 4-benzylchlorophthalazine; this crystallises in long, lustrous needles, and melts at 152° .
E. C. R.

Indigotintrisulphonic and Indigotintetrasulphonic acids. By P. JUILLARD (*Bull. Soc. Chim.* [3], 7, 619—621).—Indigotin dissolves in 30 per cent. anhydrosulphuric acid (25 parts) with a characteristic reddish-brown colour; when the product is cautiously poured into ice-cold water, and sodium chloride added to the solution, a red-brown salt, $C_{16}H_6N_2O_3(SO_3Na)_4 + 10H_2O$, separates. Its aqueous solution gives a blue precipitate on the addition of barium chloride, which, when decomposed with sulphuric acid, yields a mixture of indigotintrisulphonic and

tetrasulphonic acids. In aqueous solution, the acids dye wool and silk a bluish-red shade. A. R. L.

Carbazole. By A. MAZZARA and E. LEONARDI (*Gazzetta*, 22, ii, 569—582.—Benzoylbromocarbazole, $\text{NBz} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_3\text{Br} \end{smallmatrix}$, is obtained by brominating benzoylcarbazole in acetic acid solution. It forms small, transparent crystals, melts at 124—125° (corr.), and is very soluble in chloroform, toluene, carbon bisulphide, or benzene, but dissolves less readily in glacial acetic acid or light petroleum. On treatment with alcoholic potash, it yields the bromocarbazole, melting at 199°. On brominating carbazole, or its acetyl or benzoyl derivatives, in acetic acid solution at 100—115°, the corresponding bromo-derivative and a quantity of resinous matter are obtained, together with a substance having the composition $\text{C}_{12}\text{H}_8\text{NBr}, \text{C}_{12}\text{H}_9\text{N}$, which forms transparent, colourless scales, melting at 193—195°. This, however, behaves towards acetic anhydride and picric acid as a mere mixture of carbazole and bromocarbazole.

Benzoyldibromocarbazole, $\text{NBz} \begin{smallmatrix} \text{C}_6\text{H}_3\text{Br} \\ | \\ \text{C}_6\text{H}_3\text{Br} \end{smallmatrix}$, prepared in a manner similar to the mono-derivative, forms transparent needles or prisms melting at 215—216° (corr.); it is soluble in chloroform or toluene, but only sparingly so in alcohol or light petroleum. On treatment with alcoholic potash, it yields *dibromocarbazole*, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_3\text{Br} \\ | \\ \text{C}_6\text{H}_3\text{Br} \end{smallmatrix}$; this substance forms small, colourless prisms, melting at 212—213° (corr.).

Benzoylnitrobromocarbazole, $\text{NBz} \begin{smallmatrix} \text{C}_6\text{H}_3\cdot\text{NO}_2 \\ | \\ \text{C}_6\text{H}_3\text{Br} \end{smallmatrix}$, prepared by nitrating benzoylbromocarbazole, forms minute, translucent, yellow needles, melting at 267—268° (corr.); it is sparingly soluble in chloroform, toluene, carbon bisulphide, alcohol, or light petroleum, and is accompanied by a small quantity of another substance melting above 200°.

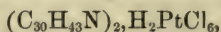
Nitrobromocarbazole, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_3\cdot\text{NO}_2 \\ | \\ \text{C}_6\text{H}_3\text{Br} \end{smallmatrix}$, is obtained by boiling its benzoyl derivative with alcoholic potash. It forms small, hard, yellow needles, which begin to sublime at 225°, and melt at 288—289° (corr.); it is soluble in acetic acid or benzene, sparingly so in alcohol or ether. Its *acetyl* derivative, $\text{NAc} \cdot \text{C}_{12}\text{H}_8\text{Br} \cdot \text{NO}_2$, forms small, whitish crystals, which rapidly turn yellow on exposure to light, and melt at 236—237° (corr.); it is soluble in benzene, but only sparingly so in alcohol or light petroleum.

Benzoylnitrobromocarbazole, identical with that described above, is obtained by brominating benzoylnitrocarbazole; the nitrobromocarbazole derived from the former substance would seem to contain both the bromine and the nitro-group in the para-position relatively to the imidogen group. From a consideration of the work of Blank (*Abstr.*, 1891, 571), it is very probable that the nitrocarbazole pre-

pared by the authors (Abstr., 1892, 616) also contains the imidogen and nitro-groups in the para-position relatively to each other.

W. J. P.

A New Acridine and an Acridylpropionic acid. By A. VOLPI (*Gazzetta*, 22, ii, 549—556).—An *acridine*, $C_{30}H_{43}N$, is formed on heating a mixture of stearic acid, diphenylamine, and zinc chloride at 220° , and is purified by means of its hydrochloride; the free base separates from dilute alcohol in long, thin, yellow needles or crystalline laminae melting at $69-70^\circ$. It is soluble in all ordinary solvents, with the exception of water; its dilute solutions have a blue fluorescence, whilst solutions of its salts show a green fluorescence. Contact with acid vapours rapidly turns it yellow, and light also changes it. The *hydrochloride*, $C_{30}H_{43}N \cdot HCl$, forms minute needles, and is soluble in alcohol or benzene. The *platinochloride*,



is obtained in yellow crystals melting at 190° . The sulphate, $C_{30}H_{43}N \cdot H_2SO_4$, is soluble in alcohol or benzene, and melts at 149° ; all the salts are decomposed by water. The differences observed between this substance and pentadecylacridine (Abstr., 1892, 342) are very slight, and the author is comparing the two bases, in order to determine whether they are identical.

Acridylpropionic acid, $C_{13}H_8N \cdot C_2H_4 \cdot COOH$, is obtained on heating a mixture of succinic acid, diphenylamine, and zinc chloride at $180-205^\circ$, and is purified by recrystallising its sodium salt, which is then decomposed by passing carbonic anhydride through its aqueous solution. The acid forms a yellow, crystalline powder, which does not melt at 300° , is insoluble in water, benzene, ether, or chloroform, and almost insoluble in hot alcohol. It dissolves in dilute acids or alkalis; the acid solutions have a green, whilst the alkaline solutions show a blue, fluorescence. The *sodium salt*, $NaC_{16}H_{12}NO_2 \cdot 2\frac{1}{2}H_2O$, loses its water at 100° , is very soluble in water, and is insoluble in ether or benzene; it decomposes at 260° without melting. Its aqueous solution gives yellow precipitates with mercuric, mercurous, or silver salts, or picric acid; a green precipitate is obtained with copper sulphate. The *silver salt* forms yellow flocks. The *hydrochloride*, $C_{16}H_{13}NO_2 \cdot HCl$, forms fairly large crystals, which melt at 268° with previous decomposition. The *platinochloride* probably contains 1 mol. H_2O , which it loses at $115-120^\circ$; it forms microscopic, yellow crystals, decomposing at 259° .

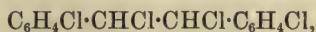
W. J. P.

Formation of Stilbene. By A. KLAGES and E. KNOEVENAGEL (*Ber.*, 26, 447—451).—When deoxybenzoïn is dissolved in a molecular proportion of benzaldehyde, and the solution saturated with hydrogen chloride, chlorobenzyldeoxybenzoïn, $COPh \cdot CHPh \cdot CHPhCl$, is formed; it crystallises from glacial acetic acid in small needles, melts at $180-182^\circ$, and a small quantity of a compound (perhaps a stereoisomeride) melting at 153° can be isolated from the mother liquor. When either of these compounds is heated, benzoic chloride and stilbene pass over. By the action of dilute alkali on chlorobenzyldeoxybenzoïn, benzamarone is obtained; whilst by adding the com-

pound to hot concentrated aqueous potash, benzylidenedeoxybenzoïn is formed. *Benzylidenedeoxybenzoïn dibromide* crystallises in nacreous leaflets or needles, and melts at 135° . *Iodobenzyldeoxybenzoïn* is prepared from deoxybenzoïn, benzaldehyde, and hydriodic acid. It melts between 155° and 170° , according to the solvent from which it is crystallised, and is probably a mixture of stereoisomerides.

A. R. L.

Condensation of Orthochlorobenzal Chloride by means of Metals. By A. H. GILL (*Ber.*, **26**, 649—652).—Orthochlorotoluene is prepared from orthotoluidine by means of the diazo-reaction; the yield is 40 per cent. of the theoretical. On treatment with chlorine at about 160° , orthochlorobenzal chloride is obtained; this boils at 228.5° ; its sp. gr. = 1.399 at 15° ; it is not acted on by sodium at 160° , and only undergoes slight change with zinc dust or finely divided copper at 100 — 110° . On heating the chloride with methyl alcohol and a mixture of equal parts of sand and finely divided silver for six hours at 95° , *orthodichlorostilbene dichloride*,



is formed, and on the addition of light petroleum to its ethereal solution, is deposited in rhombic crystals melting at 170.5° . The yield is 8 per cent. of the benzal chloride employed.

Orthodichlorostilbene, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Cl}$, is prepared by heating the preceding compound with finely divided copper at 100 — 105° , or by the action of a mixture of sand and copper on orthochlorobenzal chloride; in this case the yield is 12 per cent. of the chloride employed; the compound boils at about 220° , and is deposited from alcohol in long, colourless needles, and from toluene in rhombic prisms, which melt at 97° . Attempts to eliminate the remaining chlorine atoms were unsuccessful. By the action of chlorine, the dichloride is regenerated. On treating orthodichlorostilbene dichloride with alcoholic potash at 100° , the *trichlorostilbene*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}\cdot\text{CCl}\cdot\text{C}_6\text{H}_4\text{Cl}$, is formed, and crystallises from alcohol and ether in small scales melting at 66° . By the further action of potash on this compound, *orthodichlorotoluene*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{C}\equiv\text{C}\cdot\text{C}_6\text{H}_4\text{Cl}$, is obtained, crystallising from alcohol in colourless, rhombic plates melting at 88 — 89° .

J. B. T.

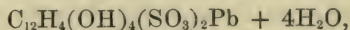
Condensation of Orthochlorobenzotrichloride by means of Metals. By F. FOX (*Ber.*, **26**, 653—656).—Orthochlorotrichlorotoluene, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CCl}_3$, is prepared by the prolonged action of chlorine on orthochlorotoluene at 130° ; the yield is 83 per cent. of the theoretical. On heating the compound in a reflux apparatus with benzene and finely divided copper for 25 hours, *orthodichlorotoluene dichloride*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CCl}\cdot\text{CCl}\cdot\text{C}_6\text{H}_4\text{Cl}$ is obtained in two modifications, which may be separated by crystallisation from light petroleum. The more sparingly soluble isomeride is deposited in needles which melt at 172° ; it boils at 209° under a pressure of 18 mm., and at 354° under ordinary pressures, being converted into the second modification to the extent of 36 per cent.

The second compound crystallises in monoclinic plates melting at 125 — 126° , and is only obtained pure, together with the compound of

higher melting point, by the action of chlorine on orthodichlorotolane in chloroform solution (compare preceding abstract); it boils at 353—356° under the ordinary atmospheric pressure, yielding 19 per cent. of the higher-melting modification, and remains unchanged on distillation in a vacuum. Both compounds yield orthodichlorotolane by the action of zinc dust at 200°. From the general properties of these compounds, the higher-melting modification is regarded as the plane symmetrical, $\begin{array}{c} \text{C}_6\text{H}_4\text{Cl}\cdot\text{CCl} \\ | \quad | \\ \text{C}_6\text{H}_4\text{Cl}\cdot\text{CCl} \end{array}$, the lower melting one as the centrisymmetrical, $\begin{array}{c} \text{C}_6\text{H}_4\text{Cl}\cdot\text{CCl} \\ | \quad | \\ \text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{Cl} \end{array}$. This view is confirmed by the fact that the former is more readily acted on by silver than the latter.

J. B. T.

Diresorcinol. By E. SELCH (*Monatsh.*, 14, 1—7).—Barth and Schreder (Abstr., 1879, 633) regarded the diresorcinol which they obtained by fusing resorcinol with soda as 3 : 5 : 3' : 5'-tetrahydroxydiphenyl, but were not able to give any proof of the relative position of the hydroxyl groups. The author endeavoured to obtain evidence as to the correctness of their view by subjecting the phenol and its tetraethyl ether to oxidation, but could not succeed in obtaining a sufficient quantity of any product for analysis. Towards sulphuric acid, diresorcinol behaves in a manner which varies according to the temperature at which the reaction is carried out; when added to 6—7 parts of sulphuric acid at 150—160°, it yields *diresorcinolsulphone*, $\text{C}_{12}\text{H}_4\text{SO}_2(\text{OH})_4$; this crystallises in colourless, silky needles, is almost insoluble in water, and carbonises above 300° without melting. Its *tetracetyl* derivative also forms silky needles, and melts at 256°. With cold sulphuric acid, diresorcinol is converted into a *disulphonic acid*, which has not been obtained pure; its *lead salt*,



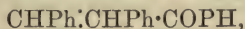
crystallises in pale-brown prisms united in small druses.

H. G. C.

Stereoisomeric Benzamarones. By E. KNOEVENAGEL and R. WEISSGERBER (*Ber.*, 26, 436—441).—Benzamarone was prepared by Japp and Klingemann's method (Abstr., 1889, 275). Assigning to it the formula $\text{COPh}\cdot\overset{*}{\text{CHPh}}\cdot\text{CHPh}\cdot\overset{*}{\text{CHPh}}\cdot\text{COPh}$, it is seen to contain two asymmetric carbon atoms, namely, those marked with an asterisk, and the authors have succeeded in separating it into two isomerides. The crude substance, mixed into a thin paste with alcohol, is digested on the water-bath for half an hour. The resinous constituents and *benzylidenedeoxybenzoin* (next abstract) are thereby dissolved. The residue is boiled for 3—4 hours with 85 per cent. acetic acid, when *isobenzamarone* separates from the filtrate on cooling. Benzamarone melts at 218—219°, and isobenzamarone resembles it in crystalline form, but is more readily soluble in alcohol, glacial acetic acid, and benzene, and melts at 179—180°. Both isomerides are structurally identical; they give the same pentaphenylpyridine (m. p. 239—240°) when heated in aqueous alcoholic solution with hydroxylamine hydrochloride at 180°.

A. R. L.

Benzylidenedeoxybenzoïn. By E. KNOEVENAGEL and R. WEISSGERBER (*Ber.*, 26, 441—446).—Benzylidenedeoxybenzoïn,



is one of the products in the preparation of benzamarone (preceding abstract). The best yield is obtained when a solution of potash (2 grams) dissolved in alcohol (5 c.c.) and water (5 c.c.), is added to a cooled solution of deoxybenzoïn (5 grams) in benzaldehyde (25 grams) and an equal volume of alcohol, and the mixture allowed to remain for 2—3 days. It forms white needles, and melts at 100°. When heated with an excess of deoxybenzoïn, benzamarone is formed; whilst if it is heated at 180° with hydroxylamine hydrochloride and alcohol, it yields a compound which crystallises in silky needles, melts at 208—209°, and, since it is insoluble in alkalis, has, perhaps,

the constitution $\begin{array}{c} \text{N}=\text{CPh} \\ | \\ \text{O} \cdot \text{CHPh} \end{array} > \text{CHPh}.$ The *hydrazone*, $\begin{array}{c} \text{CPh} - \text{CHPh} \\ | \\ \text{CHPh} \cdot \text{N} \cdot \text{NHPh} \end{array},$

is obtained by heating benzylidenedeoxybenzoïn with phenylhydrazine. Benzylidenedeoxybenzoïn and benzyl cyanide react in the presence of a small quantity of alcoholic soda, forming *benzoyltriphenylbutyronitrile*, $\text{COPh} \cdot \text{CHPh} \cdot \text{CHPh} \cdot \text{CHPh} \cdot \text{CN}$, which melts at 205—210°, and appears to be resolvable into two stereoisomerides of higher and lower melting point; the same compound is obtained from a mixture of deoxybenzoïn, α -phenylsuccinonitrile, and sodium ethoxide.

A. R. L.

Condensation of Benzaldehyde with Deoxybenzoïn. By F. KLINGEMANN (*Ber.*, 26, 818—820).—A preliminary notice, published on account of the appearance of papers by Knoevenagel, Weissgerber, and Klages (preceding abstracts). If sodium ethoxide is used as the condensing agent, four distinct products may be obtained, according to the conditions of the experiment:—(1) benzamarone, $\text{C}_{35}\text{H}_{28}\text{O}_2$; (2) benzylidenedeoxybenzoïn, $\text{C}_{21}\text{H}_{16}\text{O}$; (3) a compound, $\text{C}_{21}\text{H}_{16}\text{O}$, of unknown constitution, melting at 88—89°; (4) amaric acid, $\text{C}_{23}\text{H}_{22}\text{O}_3$, or its anhydride, $\text{C}_{23}\text{H}_{20}\text{O}_2$.

When benzamarone is distilled, it yields deoxybenzoïn, and the two isomeric substances $\text{C}_{21}\text{H}_{16}\text{O}$. That melting at 101° is an unsaturated ketone (benzylidenedeoxybenzoïn), for when reduced it yields a dihydro-product (melting at 118°), probably benzaldeoxybenzoïn, and, with phenylhydrazine, a phenylhydrazone melting at 166—167°; with deoxybenzoïn, under the influence of sodium ethoxide, it yields benzamarone. The isomeric substance melting at 88—89° is neither a ketone nor an alcohol, for it does not react either with phenylhydrazine or with acetic anhydride; it cannot be converted into benzamarone, but it can be, indirectly, into benzylidenedeoxybenzoïn.

By the action of hydrochloric acid on a mixture of deoxybenzoïn and benzaldehyde there were obtained: (1) a compound, $\text{C}_{21}\text{H}_{17}\text{OCl}$ melting at 172°; (2) an isomeric compound melting at 135°; (3) benzylidenedeoxybenzoïn; and (4) its isomeride, $\text{C}_{21}\text{H}_{16}\text{O}$. Benzylidenedeoxybenzoïn is converted into (1) and some of (2) by the action of hydrochloric acid; its isomeride, $\text{C}_{21}\text{H}_{16}\text{O}$, yields only (1).

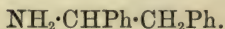
C. F. B.

Condensation of Chlorobenzile with Phenol and with Mono- and Di-methylaniline. By S. KEMPINSKI (*Bull. Soc. Chim.* [3], 7, 608—610).—When Zinin's chlorobenzile (*Annalen*, 119, 178) is heated at 60—65° with phenol (2 mols.) and some zinc chloride, hydrogen chloride is evolved, and an amorphous, red compound, soluble in alkalis, and melting at about 93°, is obtained; it is probably a *dihydroxybenzopinacolin*, $\text{COPh}\cdot\text{CPh}(\text{C}_6\text{H}_4\cdot\text{OH})_2$.

Under the same conditions, there is obtained from methylaniline a green colouring matter, which dyes cotton directly, and from dimethylaniline a blue colouring matter, which dyes wool and mordanted cotton.

A. R. L.

Reduction of Benzilehydrazone. By A. PURGOTTI (*Gazzetta*, 22, ii, 611—613).—In this preliminary note the author states that the reduction of benzilehydrazone by zinc dust and acetic acid yields a liquid base which is most probably *amidodibenzyl*,



The *sulphate* is obtained in large crystals, and is extremely soluble in alcohol; the *hydrochloride* forms white needles, and the *platinochloride* separates from its boiling aqueous solution in golden laminæ.

W. J. P.

Benzileoximes. By K. AUWERS and M. SIEGFELD (*Ber.*, 26, 788—797).—An amplification of a previous preliminary notice (*Abstr.*, 1892, 1470), with some additions. It is not true, as Minunni and Ortoleva state (this vol., i, 97), that α -benzileoxime only reacts with phenylhydrazine at 150—160°, and then yields benziledihydrazone. As before said, they react when heated at 30—40° in alcoholic solution acidified with acetic acid, and benzileoximehydrazone is formed. The other monoxime does not give this reaction; in general, it reacts much less readily than the α -oxime. It should be noted that the authors once more apply to this second oxime, which has been known for some time now as the γ -oxime, the original name of β -monoxime. The *acetyl derivative of benzileoximehydrazone*, the melting point of which was given as 109°, melts at 113° when precipitated from chloroform solution by the addition of light petroleum; after crystallisation from hot alcohol or ether, it melts at 121—122°. Perhaps these are physically isomeric modifications.

Some salts of the benzilemonoximes with bibasic acids have been prepared. These exist in two forms, represented by the formulæ

$$\alpha, \quad \begin{array}{c} \text{CPhO}\cdot\text{C}\cdot\text{Ph} \\ \parallel \\ \text{N}\cdot\text{O}-(\text{R})-\text{O}\cdot\text{N} \end{array} \quad \text{Ph}\cdot\text{C}\cdot\text{CPhO} \quad , \quad \text{and} \quad \beta, \quad \begin{array}{c} \text{Ph}\cdot\text{C}\cdot\text{CPhO} \\ \parallel \\ \text{N}\cdot\text{O}-(\text{R})-\text{O}\cdot\text{N} \end{array} \quad \text{CPhO}\cdot\text{C}\cdot\text{Ph}.$$

They are prepared by treating the dry sodium salts of the corresponding oximes (suspended in benzene) with the acid chloride. They are decomposed by alkalis into the acids and the original oximes, the α -salts much more readily than the β -ones. The *carbonates* [(R) = CO in the above formulæ] from carbonyl chloride and the sodium salts of the α - and β -oximes respectively form lustrous, white needles; the α -salt melts at 122°, the β - at 163°. The *succinates*

[$(R) = CO \cdot CH_2 \cdot CH_2 \cdot CO$], from succinic chloride, and the sodium salts of the respective monoximes, form small, prismatic, colourless crystals; the α -salt melts at 164° , the β - at 195° . C. F. B.

Oximes. By A. CLAUS (*J. pr. Chem.* [2], **47**, 139—151).—A criticism on the most recent papers of Minunni (this vol., i, 86, 89, 92, 97; compare *Abstr.*, 1892, 1080). A. G. B.

Compounds containing the Group $C_2N_2O_2$. By A. ANGELI (*Ber.*, **26**, 527—530).—*Dibenzoylglyoxime*, $NOH \cdot CBz \cdot CBz \cdot NOH$, is obtained by reducing the corresponding peroxide, $\begin{array}{c} CBz-CBz \\ || \quad || \\ N-O-N \end{array}$ (obtained by the action of nitric acid on acetophenone) with zinc dust and acetic acid. It crystallises in lustrous needles, and melts at 168° with decomposition. When treated with cold concentrated nitric acid, it is reconverted into the peroxide, which melts at 87° and has all the properties assigned to it by Hollemann (*Ber.*, **21**, 2835).

Dibenzoylazoxazole, $\begin{array}{c} CBz \cdot CBz \\ || \quad || \\ N-O-N \end{array}$, obtained by treating dibenzoylglyoxime with acetic anhydride, crystallises in large, colourless prisms, and melts at 118° . The *dioxime*, $C_{16}H_{12}N_4O_3$, crystallises in white needles, melts at 179° , dissolves easily in potash, and when treated in alkaline solution with potassium ferricyanide is converted into a compound of the composition $C_{16}H_{11}N_3O_2$, which melts at 221° . The *dihydrazone* crystallises in small, yellow needles, and melts at 172° .

Diphenyltetraketoxime, $C_6H_5 \cdot [C \cdot NOH]_4 \cdot C_6H_5$, is obtained by the prolonged action of an excess of hydroxylamine hydrochloride on a cold alkaline solution of dibenzoylglyoxime. It is a white powder and melts at 225° . E. C. R.

β -Hydroxynaphthoic acid (m. p. 216°). By H. HOSAEUS (*Ber.*, **26**, 665—673).—*Naphthophosphonic chloride*, $POCl_2 \cdot O \cdot C_{10}H_6 \cdot COCl$, is formed by the action of phosphoric chloride on hydroxynaphthoic acid; it crystallises from light petroleum in colourless needles, melts at 63° , and is extremely unstable. *β -Naphthophosphonic acid*, $PO(OH)_2 \cdot O \cdot C_{10}H_6 \cdot COOH$, is obtained by treating the preceding compound with water; it is insoluble in light petroleum, melts at 174° , and is decomposed by prolonged heating at 110° . The aqueous solution, on boiling, is resolved into β -hydroxynaphthoic acid and phosphoric acid.

β -Chloronaphthoic acid is prepared by heating the naphthoic acid (1 mol.) with phosphoric chloride (3.5 mols.) for eight hours at 180° , or by distillation of the naphthoic acid with 8 parts of phosphoric chloride; it crystallises in yellow needles, and melts at 216° . The *calcium salt* crystallises with 2 mols. H_2O .

β -Chloronaphthoic acid, on reduction with sodium amalgam, yields *α -naphthoic acid* (m. p. 160°).

Hemimellitic acid is formed by the oxidation of β -hydroxynaphthoic acid with potassium permanganate in alkaline solution.

β-Hydroxysulphonaphthoic acid, $\text{COOH} \cdot \text{C}_{10}\text{H}_5(\text{OH}) \cdot \text{SO}_3\text{H} + 4\text{H}_2\text{O}$, crystallises from dilute hydrochloric acid in pale yellow needles. The *barium salt* crystallises in colourless needles with 5 mols. H_2O .

Dihydroxynaphthoic acid, $\text{C}_{10}\text{H}_5(\text{OH})_2 \cdot \text{COOH} + \text{H}_2\text{O}$, is prepared by fusing the above sulphonic acid with potash at 260° , and crystallises from water in yellow, lustrous needles melting at 265° ; it is completely removed from solution by treatment with large quantities of animal charcoal, reduces silver solution at ordinary temperatures and alkaline copper solution on gently warming. The *diacetate* is crystalline, and melts at 188° . The *ethylic salt* is deposited in needles which melt at $148\text{--}150^\circ$. All attempts to eliminate the carboxyl group from hydroxysulphonaphthoic acid were unsuccessful.

The above results show that hydroxynaphthoic acid (m. p. 216°) is a heteronuclear compound, but it remains uncertain whether its constitution is $\text{COOH} : \text{OH} = 1' : 2$ or $4' : 2$. J. B. T.

The Azines and Eurhodoles obtained from Dihydroxydiketotetrahydronaphthalene. By T. ZINCKE (*Ber.*, 26, 613—623).—The following experiments show that the compounds obtained by the mutual action of dihydroxydiketotetrahydronaphthalene and orthodiamines are not $\beta\beta$ -naphthalene derivatives as previously supposed (*Abstr.*, 1892, 859), but belong to the $\alpha\beta$ -series; the two eurhodoles, melting at $169\text{--}170^\circ$ and $183\text{--}184^\circ$ respectively, prepared from orthotoluylenediamine and the above-mentioned diketo-compound, have, therefore, in all probability, constitutions analogous to those of the corresponding compounds prepared from phenylenediamine in the manner now to be described.

Naphthaphenazine oxide, $\text{O} < \begin{array}{c} \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{C} : \text{N} \\ | \quad \quad \quad | \\ \text{CH} \text{---} \quad \quad \text{C} : \text{N} \end{array} > \text{C}_6\text{H}_4$, is produced when dihydroxydiketotetrahydronaphthalene is treated with orthophenylenediamine in alcoholic solution; it crystallises in small, yellowish, spherical aggregates of needles, melts at $186\text{--}187^\circ$ with previous softening, and is not acted on by alkalis.

β-Hydroxynaphthaphenazine, $\begin{array}{c} \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{C} : \text{N} \\ || \quad \quad \quad | \\ \text{C}(\text{OH}) \text{---} \text{C} : \text{N} \end{array} > \text{C}_6\text{H}_4$ (*β-naphtheurhodole*), is obtained when the preceding compound is boiled with acetic acid or warmed with alcoholic hydrochloric acid, the solution diluted with water, and treated with ammonia until feebly alkaline; it crystallises in slender, intensely yellow needles, melts at $197\text{--}198^\circ$, and has both acid and basic properties. The *sodium* derivative crystallises in small, dirty-violet needles, and is only very sparingly soluble in water, but dissolves freely in alcohol, yielding a violet solution. The *hydrochloride* and the *sulphate* are brownish-red, crystalline compounds, and are only stable in presence of acids, being decomposed by water; the *platinochloride* is a reddish-brown, insoluble compound. The *acetyl* derivative, $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2$, crystallises in yellow needles, melts at $188\text{--}189^\circ$, and dissolves in concentrated hydrochloric acid with an orange-red coloration, yielding a salt which is decomposed by water;

in its hydrochloric acid solution, platonic chloride produces a sparingly soluble, red, crystalline precipitate. The *methyl* derivative, $C_{17}H_{12}N_2O$, is formed, together with large quantities of a yellow, insoluble modification of β -hydroxynaphthaphenazine, when the hydroxy-compound is treated with methylic iodide and methyl alcoholic soda; it crystallises in slender, yellow needles, melts at 158° , and is not acted on by alkalis; its *hydrochloride* crystallises in red needles, is immediately decomposed by water, and forms a brownish, granular *platinochloride*; its *bromo*-derivative crystallises in small, yellow needles, and melts at 204° .

α -Anilido- α -hydroxynaphthaphenazine, $C_{22}H_{17}N_3O$, is formed when naphthaphenazine oxide is boiled with excess of aniline in alcoholic solution. It crystallises in small, yellow needles, melts at 204 – 205° , and is readily decomposed when boiled with acids or when heated above its melting point, being converted into aniline and β -hydroxynaphthaphenazine; it is turned blue by hot alcoholic soda.

The compound of the composition $C_{22}H_{18}N_4O$, obtained by treating naphthaphenazine oxide with orthophenylenediamine under like conditions, is a yellow, granular powder, melts at 200° , and is only very sparingly soluble in the ordinary organic solvents; it readily undergoes decomposition on treatment with acids or when heated above its melting point, yielding β -hydroxynaphthaphenazine and orthophenylenediamine.

When naphthaphenazine oxide is heated with zinc dust in a stream of hydrogen, it yields a naphthaphenazine melting at 140 – 141° , identical with that obtained from the azo-derivative of β -phenylnaphthylamine.

The α -eurhodole obtained by the condensation of orthophenylenediamine and hydroxynaphthaquinone is readily converted into an acetyl derivative of the composition $C_{18}H_{12}N_2O_2$; this compound crystallises in yellowish needles, melts at 217° , and is insoluble in hydrochloric acid, which imparts to it a reddish-yellow colour.

F. S. K.

Paranthracene. By C. E. LINEBARGER (*Amer. Chem. J.*, **14**, 597–602).—When anthracene, in solution, is exposed to direct sunlight, paranthracene is formed, and separates out. If the solvent is benzene, toluene, xylene, or ethylbenzene, the solution remains colourless; if it is alcohol, acetic acid, ethylic benzoate, or benzene bromide (?), the solution becomes light yellow; whilst if it is chloroform, ethylenic bromide, or carbon bisulphide, it becomes black. In the last two cases, moreover, no paranthracene is formed, probably because the solvent itself undergoes decomposition.

For the preparation of paranthracene, xylene is the best solvent; a short exposure is then sufficient to bring about complete conversion of the anthracene. Beckmann has shown, by cryoscopic methods, that paranthracene has the formula $C_{28}H_{20}$; the author suggests that the bond between the two central carbon atoms of anthracene becomes loosed, and that two molecules then unite by the affinities thus set free, forming paranthracene.

C. F. B.

Friedel-Crafts Reaction in the Anthracene Series. By C. E. LINEBARGER (*Amer. Chem. J.*, **14**, 602—604).—Attempts to prepare phenylanthracenes by heating bromanthracene, dibromanthracene, $C_6H_4<\overset{CBr}{\underset{CBr}{|}}>C_6H_4$, and dichloranthracene, respectively, with benzene, in the presence of aluminium chloride, were unsuccessful; hydrogen bromide was indeed evolved, but no crystalline product, except anthracene itself, could be isolated. Anthracene, moreover, does not react with carbonyl chloride in carbon bisulphide solution in the presence of aluminium chloride.

C. F. B.

Valency of the Dextroterpenes in Russian Turpentine. By A. STSCHUKAREFF (*J. pr. Chem.* [2], **47**, 191—196; compare Tilden, *Trans.*, 1888, 879).—The author made several series of experiments on the absorption of bromine by pinene. Chloroform or carbon tetrachloride was used as a solvent, and the solution was either covered with a layer of water or contained in a flask provided with means for preventing the escape of hydrogen bromide. The bromination was effected either by adding a solution of bromine in the same solvent until a permanent pale yellow coloration was obtained, or by adding excess of bromine and titrating back with sodium thiosulphate. The hydrogen bromide was titrated in the aqueous solution by alkali. The results are tabulated, and the following conclusions deduced from them:—(1.) When bromine is added until coloration is produced, only 1 mol. of bromine reacts immediately with the pinene. (2.) When an excess of bromine is added, the pinene takes up 2 mols. (compare Tilden, *loc. cit.*). (3.) In both cases, hydrogen bromide is eliminated, but in smaller quantity than 1 mol., so that the action of the second molecule of bromine seems to occur according to the equation $C_{10}H_{16}Br_2 + Br_2 = C_{10}H_{15}Br_3 + HBr$. (4.) The dextroterpene in Russian turpentine may be regarded as a quadrivalent hydrocarbon, capable of combining with 2 mols. of bromine, to form a bromide which is very unstable, and rapidly loses a part of its bromine as hydrogen bromide, yielding a camphene bromide.

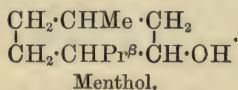
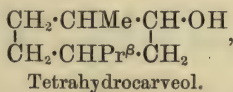
A. G. B.

Action of Acetic and Formic acids on Terebenthene. By BOUCHARDAT and OLIVIERO (*Compt. rend.*, **116**, 257—259).—Mixtures of terebenthene, acetic acid, and water, in various proportions, were allowed to remain in contact in sealed tubes at the ordinary temperature for three years. In all cases there is partial conversion of the terebenthene into an isomeric, optically-active terpine, and with the lower proportions of water, traces of terpin are formed, but the only other product is terpinenol acetate, $C_{10}H_{16} \cdot C_2H_4O_2$. Neither borneol nor isoborneol is formed. As the proportion of water increases, the rate and limit of the combination of the acid with the hydrocarbon diminishes, and when the mixture contains 25 molecular proportions of water to 1 molecular proportion of terebenthene and of acetic acid there is no combination.

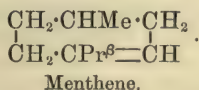
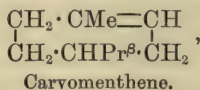
Similar experiments with formic acid show that in this case also the rate and limit of combination decrease as the proportion of water

increases, and there is no reaction when 25 molecular proportions of water are mixed with 1 molecular proportion each of terebenthene and formic acid. Formic acid is, however, more energetic in its action than acetic acid, and in this respect is comparable to the inorganic acids. When the proportion of water is low, and the acid is in excess, there is at first formation of terpinol formate, but this is attacked by the excess of formic acid with production of inactive diterpilene, a small quantity of inactive terpinene, and traces of a formate, which, on hydrolysis, yields an active borneol. With equal molecular proportions of hydrocarbon, acid, and water, a considerable quantity of terpin is formed, together with terpinene, having a rotatory power of $\alpha_D = -23^\circ 50'$, and terpinol formate of feeble rotatory power. The same products are obtained in different proportions when the proportion of water is higher. C. H. B.

Orientation in the Terpene Series. By A. BAEYER (*Ber.*, 26, 820—826).—*Dihydrocarveol*, obtained by reducing carvole with sodium in alcoholic solution, yields with acetic anhydride an *acetate* boiling at $232-234^\circ$ (corr.). This takes up hydriodic acid, and the resulting hydriodide, when reduced with zinc-dust and acetic acid, yields tetrahydrocarveol acetate, which, on saponification, yields tetrahydrocarveol, and this, on oxidation with dichromate and sulphuric acid, is converted into the corresponding ketone, *tetrahydrocarvole*. This boils at $222-223^\circ$ (corr.), and can be left in contact with permanganate for two minutes without being attacked; the *oxime* forms needles melting at $99-101^\circ$; the *hydrogen sulphite compound* is decomposed even by cold water. It is itself reduced by sodium to *tetrahydrocarveol*, a thick oil, which decomposes when distilled, but is very stable towards permanganate. Its formula follows from the known constitution of carvole; there is then only one possible formula left for its isomeride, menthol.



If tetrahydrocarveol be converted by treatment with hydrobromic acid into its bromide, and this is heated with quinoline, *carvomenthene*, boiling at $175-176^\circ$ (corr.), is obtained. It yields a dibromide, and is isomeric with the menthene obtained from menthol; the formula of the two substances must be those given below, for did the bromine atom in the bromide eliminate a hydrogen atom from the neighbouring CH_2 group, both tetrahydrocarveol and menthol would yield the same unsaturated hydrocarbon.



When limonene hydriodide, or, rather, the product of the action of

hydriodic acid (1 mol.) on limonene, is reduced with zinc-dust and acetic acid, limonene is regenerated as dipentene. The dihydriodide, under similar circumstances, yields an unsaturated hydrocarbon, which is, perhaps, identical with carvomenthene. Terpeneol hydriodide loses hydriodic acid. *Terpeneol methyl ether* was incidentally prepared, by heating terpeneol and methylic iodide in toluene solution with the liquid alloy of sodium and potassium. It boils at 207—209°, and is converted into dipentene dihydrobromide by an acetic acid solution of hydrobromic acid, even in the cold. C. F. B.

Hydroxymethylene Compounds. By L. CLAISEN (*Ber.*, 26, 725—729).—In preparing the benzoate of hydroxymethylenecamphor by treating hydroxymethylenecamphor with sodium ethoxide and benzoic chloride, the author finds that a good yield is obtained only when an absolute ethereal solution and sodium ethoxide free from alcohol are employed. When an alcoholic solution of sodium ethoxide is employed, heat is developed, and ethylic benzoate and the ethyl ether of hydroxymethylenecamphor, $C_{10}H_{14}O:CH:OEt$, are formed. The reaction takes place as follows:—The sodium ethoxide and benzoic chloride produce ethylic benzoate and sodium chloride, and the small excess of benzoic chloride which is present forms hydrogen chloride with the alcohol; then the latter effects a simple etherification of the hydroxymethylenecamphor with the alcohol. The methyl and ethyl ethers of hydroxymethylenecamphor are easily obtained by saturating the alcoholic solution with hydrogen chloride.

The methyl ether is not an oil, as stated by v. Pechmann, but a solid, which melts at 40°.

Thus, the alkyl ethers of hydroxymethylenecamphor may be obtained in three ways: (1) by etherification with alcohol and hydrogen chloride; (2) from the sodium salt and alkylic iodide; (3) from the chloride and sodium alkyloxides.

The *phenyl ether*, $C_{10}H_{14}O:CH:OPh$, obtained from the chloride and sodium phenoxide, is a viscid, colourless liquid, and boils at 214° under 13 mm. pressure.

The chloride and sodium derivative of hydroxymethylenecamphor react very easily, and yield the *anhydride* $(C_{10}H_{14}O:CH)_2O$, which melts at 188—189°. E. C. R.

Aldehydes from Terpenes. By A. ETARD (*Compt. rend.*, 116, 434—436).—Camphene, prepared by heating solid terebenthene hydrochloride with excess of lead monoxide at 110° for 24 hours, was dissolved in carbon bisulphide, and gradually mixed with two molecular proportions of chromyl dichloride, also dissolved in carbon bisulphide. An abundant precipitate is formed of the composition $C_{10}H_{16}, 2CrO_2Cl_2$, and when this is treated with water, and the solution agitated with carbon bisulphide or ether, the aldehyde is obtained. The resinous products consist chiefly of chromium camphenate.

Camphenaldehyde, $C_{10}H_{14}O$, is a solid substance, resembling camphor in appearance and consistency, and with the same property of gyratory motion on water. It is optically inactive, melts at 67°, and boils at

220°. It reduces ammoniacal silver solutions, and when exposed to air yields camphenic acid.

Camphenic acid, $C_{10}H_{14}O_2$, is volatile in water vapour, and crystallises in the condensed liquid. It melts at 65°, boils at 263–264° (uncorr.), dissolves in warm water, and forms soluble salts with magnesium, barium, calcium, and manganese, and insoluble white salts with lead, zinc, cadmium, and silver. When distilled with lime, it yields gases of the C_nH_{2n} series, hydrogen, and liquid hydrocarbons, boiling between 80° and 230°, and hence it would seem that camphenic acid is a derivative of propionic acid, and not of benzoic acid.

Terebenthene aldehyde can be obtained in the same way, and the dextro- or lævo-rotatory power of the hydrocarbon is transferred to the aldehyde. Terebenthene aldehyde boils at 205–207° under ordinary pressure; sp. gr. at 22° = 0.961. It reduces ammoniacal silver solutions, reacts with phenylhydrazine, and gives the characteristic violet coloration with a solution of magenta, decolorised by sulphurous acid (compare Abstr., 1880, 467; Trans., 1889, 45; Ber., 23, 1070).

C. H. B.

Camphorone. By W. KOENIGS and A. EPPENS (Ber., 26, 810–811; compare Abstr., 1892, 626).—*Camphorone oxime*, $C_8H_{14}C:NOH$, is obtained by boiling camphorone with hydroxylamine and sodium carbonate in solution in dilute alcohol; it crystallises in dazzling, white needles, melts at 121°, and is decomposed by boiling with alkalis or acids, or when quickly heated, an odour of phorone being observable. *Camphorone phenylhydrazone*, $C_8H_{14}C:N\cdot NHPH$, is obtained by mixing the phorone with phenylhydrazine and acetic acid in dilute alcoholic solution; it is a reddish, unstable oil, crystallising at a low temperature.

C. F. B.

Function of Camphoric acid. By A. HALLER (Compt. rend., 116, 121–123).—Phenylic isocyanate, at a temperature not exceeding 115°, acts on camphoric acid in the same way as on phthalic and succinic acids (Abstr., 1892, 1204), and yields camphoric anhydride melting at 216–217°, diphenylcarbamide, and carbonic anhydride. If, however, the tube containing the mixture is heated at 200°, the diphenylcarbamide and camphoric anhydride react with formation of symmetrical diphenylcamphoramide and carbonic anhydride. Diphenylcamphoramide can also be produced by heating a mixture of diphenylcarbamide and camphoric anhydride at 200°, but the reaction is not complete, and the diphenylcamphoramide is always mixed with unaltered diphenylcarbamide which can only be separated with difficulty. In order to obtain the pure amide, the crude product is dissolved in alcoholic potash, evaporated to dryness, and heated to incipient fusion, when the diphenylcarbamide is decomposed, but the greater part of the diphenylcamphoramide remains unaltered, and is crystallised from alcohol after removal of the potash by means of water.

Diphenylcamphoramide, $C_8H_{14}(CO\cdot NHPH)_2$, crystallises from alcohol in confused needles which melt at 221–222°, and dissolve in methyl alcohol, chloroform, and ether, but are insoluble in benzene, water,

and solutions of alkalis. It is not attacked by boiling alcoholic potash, but is partially decomposed in sealed tubes at 140—150°, with formation of phenylcamphoramic acid and aniline.

Phenylcamphoramic acid is best obtained by dissolving diphenylcamphoramide in alcoholic potash, evaporating to dryness in a silver crucible, and heating carefully to fusion as long as aniline is given off. The residue is dissolved in water, the acid liberated by the addition of an inorganic acid, and extracted with ether. It forms small, rectangular octahedra, melts at 196°, and is soluble in ether, alcohol, and potash solution, but almost insoluble in water. The isomeride obtained by Laurent by heating camphoric anhydride with aniline crystallises in needles, and melts at 209°.

The acid obtained by the author corresponds with the alkylic hydrogen salts of hydrolysis; that obtained by Laurent corresponds with the alkyl hydrogen salts obtained by direct etherification (compare Abstr., 1892, 1346).

If diphenylcarbamide and camphoric acid are heated together at 220—250°, aniline is given off, and phenylcamphoramide melting at 119° is obtained. Above 200°, therefore, diphenylcarbamide acts on camphoric anhydride in the same way as on phthalic and succinic anhydrides (*loc. cit.*).

When orthoditolylcarbamide and camphoric anhydride are heated together at 220°, in molecular proportion, *ditolylcamphoramide* is obtained; it forms small, white crystals melting at 218°.

Tetraphenylcarbamide has no action on camphoric anhydride at 220—250°.

Phenyl isocyanate, when heated at 100° with benzoic acid in molecular proportion, yields benzoic anhydride, diphenylcarbamide, and small quantities of benzanilide. If equal molecular proportions of benzoic anhydride and diphenylcarbamide are heated in sealed tubes, benzanilide is obtained in theoretical quantity. Orthotoluic acid behaves in the same way as benzoic acid.

Phenyl isocyanate is a dehydrating agent of special value in the preparation of anhydrides such as those of the acrylic series.

C. H. B.

Action of Alkali Alkyloxides on Camphoric Anhydride and other Anhydrides. By P. CAZENÈVE (*Compt. rend.*, 116, 148—151).—5 grams of sodium is dissolved in alcohol, and 20 grams of camphoric anhydride is gradually added to the solution. An energetic reaction takes place, and if the product is poured into water and subsequently acidified with hydrochloric acid, orthoethylic hydric camphorate is obtained. The alkali alkyloxide simply combines with the camphoric anhydride, with rupture of the anhydride chain. The sodium salt can be obtained as a non-crystallisable, very deliquescent syrup, very soluble in water or absolute alcohol. The methylic and amylic salts are obtained in a similar way. The latter is separated by means of light petroleum, and forms a very viscous, colourless liquid which decomposes when heated above 250°, even under reduced pressure.

Phenol under similar conditions seems to yield a camphorate.

Alkali alkyloxides react readily with phthalic and succinic anhydrides, lactide, and coumarin, but on the addition of water or alcohol of 93°, hydrolysis takes place with formation of alkali hydroxide, and disodium phthalate, succinate, or lactate is obtained. Coumarin with sodium ethoxide yields sodiocoumarin and ethyl alcohol.

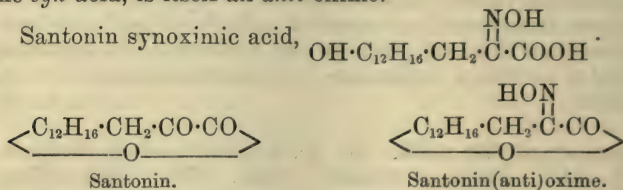
It follows that the alkylic salts of camphoric acid are less easily hydrolysed than those of phthalic and succinic acids, and camphoric anhydride is neither a lactide nor a coumarin (compare Trans., 1892, 1088—1096).
C. H. B.

Sulphocamphylic acid. By W. KOENIGS and J. HOERLIN (*Ber.*, 26, 811—817; compare Perkin, Proc., 1893, 109).—This acid, $C_9H_{16}SO_6$, is obtained by heating camphoric acid with strong sulphuric acid on the water-bath; an improved method is given for its preparation. It crystallises with $2H_2O$; two silver salts, $C_9H_{14}SO_6Ag_2$ and $C_9H_{15}SO_6Ag + H_2O$, were prepared. When the acid is heated at 210—220°, or, better, with superheated steam at 170—190°, *isolaurolic acid*, $C_9H_{14}O_2$, is obtained in white needles melting at 135°. It is a weak acid; its *calcium* and *potassium salts*, $(C_9H_{13}O_2)_2Ca + H_2O$ and $C_9H_{13}O_2K$, were prepared. It is further stated that new crystallised compounds have been obtained by the action of bromine at 100°, of alkaline permanganate, and of nitric acid respectively; the first melts at 181—182°, and contains bromine, but no sulphur; the third melts at 198° with decomposition, and appears to have the composition $C_6H_{10}O_5$. Sulphocamphylic acid is probably a true sulphonic acid, for it is very stable when treated with nitric, hydrochloric, or hydrobromic acid, only traces of sulphuric acid being formed.

A good method is given for preparing the anhydrides of bibasic acids. It is to heat them with acetic anhydride (1 mol.) containing a little zinc chloride, and wash the product with water and cold aqueous sodium carbonate.
C. F. B.

Santoninoxime and Santoninoximic acids. By J. KLEIN (*Ber.*, 26, 411—414; compare this vol., i, 111—112).—A further proof is adduced of the author's view that the carbonyl group which determines the ketonic nature of santonin is situated in the side chain. The proof depends on the fact that two oximic acids, but only one oxime, are known. The oxime, prepared according to Gucci's method (*Abstr.*, 1890, 902), contains 1 mol. H_2O , and melts at 199—201°. If prepared by hydrolysing the acetate (which melts at 165—170°), or by treating an alkaline solution of santonin with hydroxylamine hydrochloride and then acidifying, it melts at 207—209°. Both varieties have the same appearance, and are, in fact, chemically identical, for they yield identical acetyl and benzyl derivatives. The oxime is moreover a normal one, for its benzyl derivative (melting at 151—152°) yields benzyl iodide when heated with hydriodic acid. Now when santoninoxime is prepared in alkaline solution, and the solution, containing an alkaline salt of the oximic acid, is treated with ferric chloride, the violet-red colour characteristic of *syn*-oximic acids is obtained; but if the already prepared oxime is dissolved in alkali and the solution acidified and treated with ferric chloride, a

yellow colour only is produced. Hence there are two oximic acids, and that formed by direct oximation is the *syn*-oximic acid. From this it follows that the CO group of santonin is in the side chain, and further that santoninoxime, since it yields an oximic acid isomeric with the *syn*-acid, is itself an *anti*-oxime.

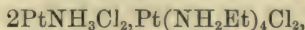


It will be noted that many of the melting points quoted above differ considerably from those given by Gucci. C. F. B.

Klein's View of the Structure of Santonin. By S. CANNIZZARO (*Ber.*, 26, 786—788).—The author expresses surprise that Klein (preceding abstract) still persists in thinking that santonin contains a CO group, together with three carbon atoms in the side chain. He maintains that the formula $\text{CH}_2 \cdot \text{CMe} \cdot \overset{\text{CO} \cdot \text{CMe} : \text{C}}{\underset{\text{||}}{\text{C}}} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \overset{\text{CH} - \text{CHMe}}{\underset{\text{||}}{\text{C}}} \cdot \text{CH} \cdot \text{O} \cdot \text{CO}$ best expresses the hitherto known reactions of santonin, whilst many of these are not explained by Klein's formula. C. F. B.

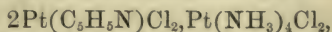
New Series of Basic Platinum Compounds. By A. COSSA (*Gazzetta*, 22, ii, 620—635; compare *Abstr.*, 1890, 1218).—*Platososemiamine platosodipyridine chloride*, $2\text{PtNH}_3\text{Cl}_2, \text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$, separates on mixing solutions of platososemiamine potassium chloride and platosodipyridine chloride; it crystallises from boiling water in anorthic prisms ($\alpha = 51^\circ 20'$, $\beta = 111^\circ 18'$, $\gamma = 88^\circ 18'$). On treatment with a solution of potassium platinochloride, K_2PtCl_4 , a reddish precipitate of platosodipyridine platinochloride falls, whilst platososemiamine potassium chloride remains in the mother liquor. With platosodiamine chloride, it yields the previously described salt of the composition $2\text{PtNH}_3\text{Cl}_2, \text{Pt}(\text{NH}_4)_4\text{Cl}_2$, together with platosodipyridine chloride. On adding sodium platinochloride to its solution, platindipyridine platinochloride, $\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_4, \text{PtCl}_2$, is precipitated.

Platososemiamine platosodiethylamine chloride,



is deposited on mixing hot concentrated solutions of platososemiamine potassium chloride and platosodiethylamine chloride. It forms anhydrous, pleochromatic, orthorhombic prisms, and its behaviour towards reagents is quite analogous to that of the preceding salt.

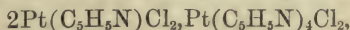
Platososemipyridine platosodiamine chloride,



is formed, together with other products, on adding pyridine to an aqueous solution of potassium platinochloride; it is sparingly soluble in cold water, and is obtained in thin, rhombohedral laminæ. On

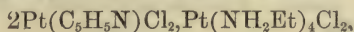
further treatment with potassium platinochloride, Magnus' salt is deposited, and *platosemipyridine potassium chloride*, $\text{Pt}(\text{C}_5\text{H}_5\text{N})\text{Cl}_2 \cdot \text{KCl}$, which crystallises in orthorhombic prisms, remains in solution. This substance is reconverted into the original double salt by the addition of platosodiamine chloride, and yields platosodipyridine chloride when treated with excess of pyridine.

Platosemipyridine platosodipyridine chloride,



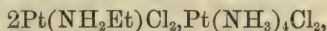
is precipitated on mixing solutions of platosodipyridine chloride and platosemipyridine potassium chloride or platosemipyridine platosodiamine chloride. It is also obtained by heating platosemipyridine chloride with dilute hydrochloric acid and subsequently adding platosodipyridine chloride; the yield is, however, poor. It forms minute, doubly-refracting, acicular, yellow crystals, and, on treatment with pyridine, gives platosodipyridine chloride.

Platosemipyridine platosodiethylamine chloride,



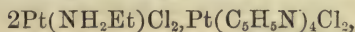
is obtained, together with platosemidipyridine chloride, on adding pyridine to hot aqueous potassium platinochloride. It forms small, yellow prisms, and is sparingly soluble in cold water; it yields platosemipyridine platosodipyridine chloride when treated with platosodipyridine chloride, and on adding excess of potassium platinochloride, platosodiethylamine platinochloride separates, whilst platosemipyridine potassium chloride remains in solution.

Platosemiethylamine platosodiamine chloride,



obtained in a manner analogous to the preceding salts, forms thin, monosymmetric prisms, and is soluble in water, but insoluble in alcohol. It yields Magnus' salt and platosemiethylamine potassium chloride when treated with potassium platinochloride; excess of ethylamine converts it into a mixture of the chlorides of platosodiamine and platosodiethylamine.

Platosemiethylamine platosodipyridine chloride,



separates on mixing solutions of the preceding salt and platosodipyridine chloride. It forms yellow, fragile, opaque, orthorhombic crystals, $a : b : c = 1.478 : 1 : 4.542$.

The formation of the above salts confirms the view that platinum can unite with a single molecule of a base to form compounds homologous to the monammoniacal platinum derivatives previously investigated by the author.

W. J. P.

So-called Quinolinium Bases. By H. DECKER (*J. pr. Chem.* [2], 47, 222—235).—The author replies to the points raised by Roser (this vol., i, 177), and criticises the analytical numbers which were published by Claus in his paper on derivatives of cinchonic acid (Abstr., 1892, 1488).

A. G. B.

Nitro-derivatives of Isoquinoline. By A. CLAUS and K. HOFFMANN (*J. pr. Chem.* [2], 47, 252—266).—1- (or 4-) *Nitroisoquinoline* is the sole product of the nitration of isoquinoline with nitric acid (1 mol.) and sulphuric acid in the cold. At higher temperatures and with a larger proportion of nitric acid, the dinitro-product is obtained. 1-Nitroisoquinoline crystallises in long, slender, yellowish needles, melts at 110°, sublimes when carefully heated, and dissolves in most solvents except cold water. It is somewhat basic; the *hydrochloride*, $C_9H_6N_2O_2 \cdot HCl$, crystallises in anhydrous, prismatic, transparent, yellow tables, and melts to a black mass at 245°; the *sulphate*, $(C_9H_6N_2O_2)_2H_2SO_4$, melts with blackening at 174°; the *nitrate* becomes dark and melts at 198°; the *platinochloride* decomposes at 330°. The *methiodide*, $C_9H_6N_2O_2 \cdot MeI$, melts, with decomposition, at 205°; the *methochloride* decomposes at 225—227°. These metho-derivatives yield the same base whether decomposed by ammonia or silver oxide, and the hydrochloride of the base is identical with the methochloride (compare Abstr., 1891, 1252). Oxidation of 1-nitroisoquinoline yields nitrophthalic acid $[NO_2 : (COOH)_2 = 3 : 1 : 2]$ (m. p. 220°).

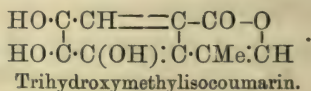
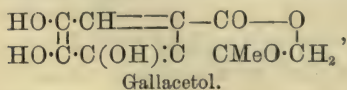
1- (or 4-) *Amidoisoquinoline*, obtained by reducing the nitro-derivative in the usual way, crystallises in colourless needles or nacreous plates, and melts at 128°. The *hydrochloride*, $C_9H_6N_2 \cdot HCl$, melts with blackening at 220°; the *platinochloride* decomposes at 200°.

1- (or 4-) *Bromisoquinoline* is prepared from the amido-derivative by the diazo-reaction. It crystallises in colourless, vitreous needles, and melts at 80.5° (compare Abstr., 1891, 580). The *nitrate*, $C_9H_6BrN \cdot HNO_3$, melts at 193°. The *nitro-derivative* crystallises in colourless needles, and melts at 140°. The *methiodide*, $C_9H_6BrN \cdot MeI$, crystallises in yellow columns, and melts at 274°. When this methiodide is treated with silver oxide, it gives a strongly alkaline base which is soluble in water but insoluble in ether, and yields the original methohaloid when treated with acids; but caustic alkalis (except ammonia) convert the methiodide into a base which is insoluble in ether and is reconvertible into a haloïd dissimilar from the original methohaloid.

Dinitroisoquinoline forms small, yellowish, lustrous crystals, melts at 233.5°, and is sparingly soluble in alcohol; the *platinochloride* and *methiodide* have been prepared.

A. G. B.

Syntheses of Isocumarin and Isoquinoline Derivatives. By P. FRITSCH (*Ber.*, 26, 419—422).—If gallacetol, obtainable from gallic acid (?) and chloracetone, is rendered anhydrous and then mixed with cooled concentrated sulphuric acid, condensation takes place, and a *trihydroxymethylisocoumarin* is formed.



This substance crystallises in efflorescent tables. When heated in a sealed tube with alcoholic ammonia at 120—130°, NH is substituted for

the -O- atom, and a substance is formed which would be called *trihydroxymethylisocarbostyryl*, according to Bamberger's nomenclature, but which the author proposes to name *trihydroxymethylisoquinolone*.

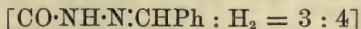
Other attempts at analogous syntheses have so far been unsuccessful. C. F. B.

Pyrazolone and some Derivatives. By R. v. ROTHENBURG (*Ber.*, 26, 415—417; compare this vol., i, 180).—*Ethyl*ic 4-azobenzene-pyrazolone-3-carboxylate, $\text{NH} \begin{array}{c} \text{N}=\text{C} \cdot \text{COOEt} \\ | \\ \text{CO} \cdot \text{C} : \text{N}_2\text{HPh} \end{array}$, was prepared by treating ethylic pyrazolone-3-carboxylate with a diazobenzene salt; it melts at 241°, forms sparingly soluble red plates, and has acid properties. By treating an alcoholic solution of the same ethylic salt with nitrous anhydride, *ethylic isonitrosopyrazolonecarboxylate*



was obtained; this forms yellowish, ill-defined crystals, and melts at 182°; its *silver salt* is a reddish-yellow powder. The same ethylic salt, when treated with benzaldehyde, yields *ethylic benzalpyrazolonecarboxylate* $[\text{COOEt} : \text{CHPh} = 3 : 4]$ as a reddish-yellow, very sparingly soluble substance melting above 250°.

If pyrazolone-3-carbonylhydrazine is shaken with benzaldehyde in aqueous solution, *pyrazolonecarbonylbenzalhydrazine*



is obtained as a white, sparingly soluble substance melting above 250°. If excess of benzaldehyde is present, *benzalpyrazolonecarbonylbenzalhydrazine* $[\text{CO} \cdot \text{NH} \cdot \text{N} : \text{CHPh} : \text{CHPh} = 3 : 4]$ is formed; it is a yellowish, very sparingly soluble powder melting above 250°.

Silver pyrazolonecarboxylate $[\text{COOAg} : \text{HAg} = 3 : 4]$ forms a white, unstable powder. The acid, when treated with a diazobenzene salt, yields *azobenzene-pyrazolonecarboxylic acid* $[\text{COOH} : \text{N} \cdot \text{NHPh} = 3 : 4]$ as a fine powder melting above 250°. And the same acid, when suspended in alcohol and treated with gaseous nitrous acid, yields *isonitrosopyrazolonecarboxylic acid* $[\text{COOH} : \text{NOH} = 3 : 4]$ as golden-yellow plates decomposing at 215—220°; the *silver salt* of this, containing 2 atoms of silver in the molecule, forms an orange-yellow powder which explodes when heated. Again, the same acid yields, with benzaldehyde, at 120—150°, or under the action of strong hydrochloric acid, *benzalpyrazolonecarboxylic acid* $[\text{COOH} : \text{CHPh} = 3 : 4]$ as a yellow, amorphous powder melting at 243°. C. F. B.

Condensation Products of the Hydrazides of Ethyl Acetoacetate and Oxalacetate. By C. WALKER (*Amer. Chem. J.*, 14, 576—586).—The hydrazide of ethylic acetoacetate,



can yield, under different conditions: (I) 1-phenyl-3-methyl-5-pyrazolone (Knorr, *Abstr.*, 1887, 601; Nef, 1892, 145); (II) 1-phenyl-3-methyl-5-ethoxypyrazole, $\begin{array}{c} \text{CMe} \\ || \\ \text{CH} : \text{C}(\text{OEt}) \end{array} > \text{NPh}$; and (III) ethylic

α -methylindole- β -carboxylate (Nef, Abstr., 1892, 142). The hydrazide of ethylic oxalacetate, $\text{COOEt}\cdot\text{CH}\cdot\text{C}(\text{COOEt})\cdot\text{NH}\cdot\text{NHPh}$, behaves in a similar manner, except that no compound analogous to (III) has yet been obtained.

That the salt III (which is obtained by the action of strong sulphuric acid on the hydrazide and melts at 131° , and not at 134° as previously stated) has the constitution $\text{NH}\langle\text{CMe}\rangle_{\text{C}_6\text{H}_4}\text{C}\cdot\text{COOEt}$, was proved by its having the same properties as the ethylic salt prepared, for purposes of comparison, from the α -methindole- β -carboxylic acid of Ciamician and Magnanini (Abstr., 1888, 958). It gives no coloration with ferric chloride, and is stable towards alcoholic potash, but if heated with caustic potash it loses carbonic anhydride, and forms methylketole.

The compound (II) is obtained by treating ethylic acetoacetate with phenylhydrazine hydrochloride (compare Freer, Abstr., 1892, 953, and this vol., i, 67, who describes it, probably erroneously, as a phenylmethylpyrazolone). Its properties closely resemble those of the phenylethoxypyrazole mentioned above. The *platinochloride* forms yellow, six-sided prisms melting at 191° .

When the hydrazide of ethylic oxalacetate is treated with dehydrating agents, the chief product is a compound analogous to (I), but at the same time another, analogous to (II), is formed in small quantity—in largest amount when an acetic acid solution of the hydrazide is saturated with hydrogen chloride and warmed for an hour at 60° . It crystallises in needles, melts at $83\text{--}84^\circ$, and has feebly basic properties.

Its constitutional formula is $\text{C}(\text{COOEt})\cdot\text{N}\langle\text{CH}=\text{C}(\text{OEt})\rangle\text{NPh}$. The COOEt group may be hydrolysed by boiling with alcoholic potash, and 1-phenyl-5-ethoxypyrazole-3-carboxylic acid, $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3$ is then obtained. This forms transparent plates or flat needles, which become opaque when dried, and melt at $152\text{--}153^\circ$; the *barium salt*, with $2\text{H}_2\text{O}$, forms colourless needles; the *calcium salt*, with $4\text{H}_2\text{O}$, rhombic plates. When the acid, or the ethylic salt, is heated with strong hydrochloric acid at 150° in a sealed tube, the OEt group is also saponified, and 1-phenyl-5-hydroxypyrazolecarboxylic acid, $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_3$, is formed. This forms colourless needles melting at $252\text{--}253^\circ$; when heated to 230° , it loses carbonic anhydride and chars; its *silver salt*, $\text{C}_{10}\text{H}_6\text{N}_2\text{O}_3\text{Ag}_2$, forms a colourless, gelatinous precipitate. The ethylic salt, when heated at $205\text{--}230^\circ$, loses carbonic anhydride and yields 1-phenyl-5-ethoxypyrazole as a dark red oil of feebly basic properties, which forms a *platinochloride*, $(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O})_2\cdot\text{H}_2\text{PtCl}_6$, as pale yellow needles melting at $142\text{--}143^\circ$.

C. F. B.

Benzo-3-phenylpyridazolone By R. v. ROTHENBURG (*Ber.*, 26 417—419).—This substance, $\text{CH}\cdot\text{CH}\cdot\text{C}\cdot\text{CPh}\cdot\text{N}\langle\text{CH}\cdot\text{CH}\cdot\text{C}\cdot\text{CO}\cdot\text{NH}\rangle$, is formed when

orthobenzoylbenzoic acid, or, better, its ethylic salt, is heated with hydrazine hydrate in alcoholic solution. It forms flat needles, melts at 232° , and distils unchanged, but is decomposed by acids and alkalis into the above components. The imido-group does not react

with nitrous acid, but its hydrogen atom can be replaced by methyl if the substance is heated with methylic iodide and methyl alcohol in a sealed tube at 100°; the product forms plates which melt at 153°, and are more soluble than the mother substance. C. F. B.

Phenyluracil and its Analogues. By E. WARMINGTON (*J. pr. Chem.* [2], **47**, 201—221).—*Phenyluracil*, $\text{OH}\cdot\text{C}\begin{smallmatrix} \text{N}=\text{CPh} \\ \text{N}\cdot\text{C}(\text{OH}) \end{smallmatrix}\text{CH}$, is made by heating ethylic benzoylacetate with carbamide at 170°. It crystallises in small rhombohedra, melts at 262·5°, and dissolves easily in warm alcohol, glacial acetic acid, and boiling water; it has feebly acid properties, dissolving in alkalis with formation of salts. The *silver* salt, $\text{C}_{10}\text{H}_6\text{Ag}_2\text{N}_2\text{O}_2$, was analysed, and the *calcium* salt crystallised. Strong hydrochloric acid, methylic iodide, and hydroxylamine are without action on it. When heated with phosphoric chloride, it yields *phenyldichlorometadiazine*, $\text{CCl}\begin{smallmatrix} \text{N}:\text{CPh} \\ \text{N}\cdot\text{CCl} \end{smallmatrix}\text{CH}$, which crystallises in laminæ, melts at 86·5°; and is reconverted into phenyluracil when heated with strong hydrochloric acid at 160°. The latter fact confirms the constitution here ascribed to phenyluracil (which also finds support in the indifference of methylic iodide) and confutes Behrend's view (*Annalen*, **229**, 25) that these compounds are dicarbonyl derivatives. By heating phenyldichlorometadiazine with alcoholic ammonia, *phenyldiamidometadiazine hydrochloride*, $\text{C}_{10}\text{H}_{10}\text{N}_4\cdot 2\text{HCl}$, was prepared; it crystallises in lustrous needles, and decomposes at 290°.

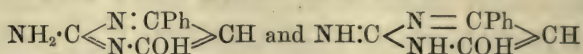
Phenylthiouracil, $\text{SH}\cdot\text{C}\begin{smallmatrix} \text{N}=\text{CPh} \\ \text{N}\cdot\text{C}(\text{OH}) \end{smallmatrix}\text{CH}$, is similarly prepared from ethylic benzoylacetate and thiocarbamide; it crystallises in bright yellow needles, melts at 253—254° (uncorr.), and dissolves in warm dilute alkalis, alcohol, and glacial acetic acid. A *silver* salt, containing 2 atoms of silver, was prepared. Strong hydrochloric acid at 180°, and fuming nitric acid at the ordinary temperature, convert it into phenyluracil.

The reaction between diphenylthiocarbamide and ethylic benzoylacetate at 180° yields benzoylactic anilide (m. p. 107—109°; Knorr, *Abstr.*, 1888, 1113); distillation with potash converts this substance into acetophenone, aniline, potassium carbonate, and diphenylcarbamide.

Ethylic benzoylacetate had no action on diphenylthiocarbamide in ether at 160°, or on monophenylcarbamide at 150—160°.

"Phenylimidouracil" was obtained by Jaeger (*Abstr.*, 1891, 1007) by the mutual action of guanidine carbonate and ethylic benzoylacetate, and was found to melt at 294°. The same compound is obtained by the action of alcoholic ammonia on phenylthiouracil. When the mother liquor from the guanidine reaction was heated in a tube at 160°, and then evaporated to dryness and extracted with dilute hydrochloric acid, the hydrochloride of an isomeride of Jaeger's base was obtained. The new *base* melts at 272—274°, and crystallises in long, rhombohedral plates; it is almost twice as soluble in absolute alcohol at 26·5° as is Jaeger's base, and its hydrochloride melts at

276—277°, whereas that of “phenylimidouracil” melts at 269°. The *picrate* of the base of m. p. 294° melts at 240—241° (uncorr.); that of the other base melts at 241—242°, but each *picrate* yields its own base when treated with ammonia. The *nitrates* were also prepared, and found to be very similar. Both bases yield an *acetyl* derivative, which melts at 248° (uncorr.), but this derivative, when decomposed with potash, always yields the base which melts at 294°, from whichever base it may have been originally made. Strong hydrochloric acid at 190—200° converts both bases into phenyluracil and ammonium chloride. Nitrous acid also converts them into phenyluracil. The bases readily pass into each other; thus that of higher melting point is largely converted into that of lower melting point when heated with alcohol at 180°. The author is of the opinion that the two bases are to be represented by the formulæ



respectively, but he is at present unable to identify either of them.

A. G. B.

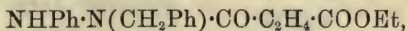
***β*-Succinylphenylhydrazide or 1-Phenyl-3:6-orthopiperazone.**

By A. MICHAELIS and R. HERMENS (*Ber.*, **26**, 674—680).—The production of phenylorthopiperazone from succinic chloride and sodium phenylhydrazine (Abstr., 1892, 1494) takes place in two stages; in the cold, sodium chloride, phenylorthopiperazone, and phenylhydrazine hydrochloride are formed, and then, on heating, the phenylhydrazine hydrochloride and excess of succinic chloride react to yield a further quantity of phenylorthopiperazone and hydrogen chloride. The phenylorthopiperazone is therefore obtained by boiling a mixture of phenylhydrazine hydrochloride, succinic chloride, and benzene in a reflux apparatus as long as hydrogen chloride is evolved.

1-Phenyl-3:6-orthopiperazone, $\text{C}_2\text{H}_4 \begin{array}{c} \text{CO}\cdot\text{NPh} \\ \text{CO}\cdot\text{NH} \end{array}$, when heated with hydrochloric acid or alkalis, is converted into phenylhydrazine and succinic acid. It distils without decomposition at 240° under 10 mm. pressure, but is converted into *α*-succinylphenylhydrazide when distilled under the ordinary pressure. When distilled with zinc dust, it yields aniline, *α*-succinylphenylhydrazide, and a viscid oil, which the authors believe to be phenylorthopiperazine. The salts of phenylorthopiperazone are soluble in water; the silver and copper salts are crystalline, the lead and barium salts gummy. The *benzoyl* compound crystallises in white leaflets, and melts at 185°. Alkyl derivatives are easily obtained by the action of alkylic iodides on the silver or sodium salts. *Phenylmethylpiperazone*, $\text{C}_2\text{H}_4 \begin{array}{c} \text{CO}\cdot\text{NPh} \\ \text{CO}\cdot\text{NMe} \end{array}$, melts at 180°.

The *ethyl* compound forms colourless crystals, melts at 60·5°, is decomposed when heated with alkalis, and reduces Fehling's solution on boiling. The *benzyl* compound crystallises in colourless needles, and melts at 159°.

Ethylic phenylbenzylhydrazinesuccinate,



crystallises from the mother liquor obtained in the preparation of the preceding phenylbenzylpiperazone, and melts at 79° . It is easily hydrolysed by heating with alcoholic potash, and yields *phenylbenzylhydrazinesuccinic acid*. This crystallises in long, colourless needles, melts at 142° , and energetically reduces Fehling's solution when warmed.

The authors believe that they have obtained symmetrical *benzylphenylhydrazine*, $\text{NPh}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, by heating the preceding compound with concentrated hydrochloric acid in a reflux apparatus. It crystallises in colourless leaflets, melts at $167\text{--}170^\circ$, and on oxidation with yellow mercuric oxide, yields an oil which is probably phenylazobenzyl, $\text{PhN}:\text{N}\cdot\text{CH}_2\text{Ph}$, together with a sparingly soluble compound melting at $200\text{--}201^\circ$. Unsymmetrical benzylphenylhydrazine also melts at 167° , but it crystallises in needles, and yields a tetrazone when treated with mercuric oxide.

E. C. R.

Action of Ammonia and Hydrazine on Opianic and Phthalaldehydic acids. By C. LIEBERMANN and A. BISTRZYCKI (*Ber.*, 26,

531—540).—*Dimethoxyphthalazone* (*opiazone*), $\text{C}_6\text{H}_2(\text{OMe})_2 < \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CH}:\text{N} \end{smallmatrix}$,

is obtained by warming an aqueous solution of opianic acid, hydrazine sulphate, and sodium acetate on the water bath. It crystallises from water in beautiful, long needles, containing 1 mol. H_2O , melts at 162° , loses its water at 100° , and then melts at 166° . It dissolves both in strong hydrochloric acid and potassium hydroxide, and is precipitated on the addition of water. It is not acted on by Fehling's solution. When dissolved in concentrated sulphuric acid, and treated with nitric acid, it yields a compound crystallising in yellow needles. The *methyl* compound, obtained by the action of methylic iodide on the potassium salt, crystallises in needles, and melts at 138° . The *acetyl* derivative crystallises in needles, and melts at $158\text{--}159^\circ$.

Dichlorodihydro-opiazine, $\text{C}_6\text{H}_2(\text{OMe})_2 < \begin{smallmatrix} \text{CCl}_2\cdot\text{NH} \\ \text{CH}:\text{N} \end{smallmatrix}$, is obtained by the action of phosphorus pentachloride on the preceding compound. It crystallises in yellow aggregates, melts at 260° with decomposition, and when treated with water, or better with dilute soda, is converted into *monochloro-opiazine*, $\text{C}_6\text{H}_2(\text{OMe})_2 < \begin{smallmatrix} \text{CCl}\cdot\text{N} \\ \text{CH}:\text{N} \end{smallmatrix}$. This melts at 152° , is very easily decomposed, and on reduction yields an oily base free from chlorine, which quickly turns brown.

Diopianhydrazonic anhydride, $\begin{smallmatrix} \text{N}:\text{CH}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{CO} \\ \text{N}:\text{CH}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{CO} \end{smallmatrix} > \text{O}$, is obtained, together with opiazone, when a solution of opianic acid, hydrazine sulphate, and sodium acetate is heated to boiling for a few minutes. It is a heavy, white, crystalline powder, melts at 225° , is insoluble in alkali, and has no action on Fehling's solution.

Phthalazone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \diagup \quad \diagdown \\ \text{CH} : \text{N} \end{smallmatrix}$, is obtained from phthalaldehydic acid, in the same way as opiazone from opianic acid. It crystallises in long, lustrous needles, melts at $183\text{--}184^\circ$, sublimes at 100° in small prisms, and closely resembles opiazone. The *silver salt*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NAg} \\ \diagup \quad \diagdown \\ \text{CH} : \text{N} \end{smallmatrix}$, crystallises in aggregates of microscopic needles. The *acetyl compound* crystallises in small prisms, and melts at $132\text{--}133^\circ$.

Diphthalaldehydhydrazonic acid, $\text{N}_2(\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH})_2$, is obtained by mixing cold, saturated solutions of phthalaldehydic acid and hydrazine acetate. It crystallises in pale yellow, microscopic needles, melts at 211° , is without action on Fehling's solution, and when boiled with water is converted into phthalaldehydic acid and phthalazone. The *silver salt* is obtained as a white, flocculent precipitate.

When opianic acid is heated with alcoholic ammonia for 6—8 hours at 160° , or with aqueous ammonia for 2—3 days at the temperature of boiling water, *bisdimethoxymetindolone* and *tetramethoxydihydrodiphthalylldiimide* are formed. The two compounds are separated by means of acetic acid, in which the former is insoluble.

Bisdimethoxymetaindolone, $(\text{OMe})_2\text{C}_6\text{H}_2 \cdot \text{C} \equiv \text{C} \cdot \text{C}_6\text{H}_2(\text{OMe})_2$, $\text{OH} \cdot \text{C} \equiv \text{N} \quad \text{N} \equiv \text{C} \cdot \text{OH}$, is nearly insoluble in all solvents, does not melt at 340° , is a very indifferent compound, and exhibits in concentrated sulphuric acid a deep rose-red coloration and fluorescence, which changes to a beautiful blue on the addition of nitric or chromic acid.

Tetramethoxydihydrodiphthalylldiimide, $\text{C}_2\text{H}_2[\langle \text{C}_6\text{H}_2(\text{OMe})_2 \rangle_{\text{NH} \text{---} \text{CO}}]_2$, crystallises in small, bright yellow needles, melts at 249° with decomposition, and has feeble basic properties. With concentrated sulphuric acid, it gives a yellow solution, which does not turn blue on the addition of nitric acid.

The action of ammonia on phthalaldehydic acid is very similar to its action on opianic acid, and the two following compounds were obtained.

Bismetaindolone, $\text{OH} \cdot \text{C} \leq \text{C}_6\text{H}_4 \rangle \text{C} : \text{C} \langle \text{C}_6\text{H}_4 \geq \text{C} \cdot \text{OH}$, is very sparingly soluble, crystallises in microscopic prisms, does not melt at 330° , and exhibits in concentrated sulphuric acid a yellow coloration, which changes to dirty brown on the addition of nitric acid.

Dihydrodiphthalylldiimide, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle_{\text{NH}} \text{CH} \cdot \text{CH} \langle \text{C}_6\text{H}_4 \rangle_{\text{NH}} \text{CO}$, is easily soluble in acetic acid, crystallises in colourless needles, and melts at 284° with decomposition.

The authors attempted to prepare the last two compounds by heating diphthalyl with methyl alcoholic ammonia at 160° ; the compound obtained, however, was diphthalylmonoimide. E. C. R.

Derivatives of Dichloroquinazoline. By A. KÖTZ (*J. pr. Chem.* [2], 47, 303).—When $\beta\delta$ -dichloroquinazoline (Abstr., 1889,

610) is heated with alcoholic ammonia at 150° , the compound $C_6H_4 < \begin{smallmatrix} C(NH_2):N \\ N:C(NH_2) \end{smallmatrix} >$ is formed; it crystallises in long, yellowish needles, and melts at $248-250^{\circ}$; a *platinochloride* was obtained. The corresponding *methylamine derivative* melts at $282-284^{\circ}$, and yields a *platinochloride*. By heating the dichloroquinazoline with an alcoholic solution of potassium hydrogen sulphide, a *dithio-derivative*, $C_8H_6N_2S_2$, is obtained; it melts above 250° , is decomposed at 260° , and gives a white precipitate with mercuric chloride. A. G. B.

Pyrazine. By L. WOLFF (*Ber.*, 26, 721—725).—Pyrazinetetracarboxylic acid, $C_4N_2(COOH)_4 + 2H_2O$, is obtained by oxidising tetramethylaldine with potassium permanganate (*Ber.*, 20, 427). It crystallises in white leaflets, melts at $204-205^{\circ}$ with decomposition, and gives a violet to cherry-red coloration with ferrous sulphate, which disappears on the addition of a mineral acid. The normal potassium and sodium salts are easily soluble in water; the *barium* $C_8N_2O_8Ba_2 \cdot 1\frac{1}{2}H_2O$, the *calcium*, with $2\frac{1}{2}H_2O$, and *silver salts*, with $\frac{1}{2}H_2O$, are almost insoluble. The *dipotassium* and *disodium salts*, $C_4N_2(COONa)_2(COOH)_2 + 2H_2O$, are very characteristic, and sparingly soluble in cold water. The dipotassium salt, when heated with water at 200° , yields carbonic anhydride, pyrazine, and pyrazinedicarboxylic acid.

Pyrazinedicarboxylic acid, $C_4N_2H_2(COOH)_2 + 2H_2O$, crystallises in prisms, and volatilises without melting when heated at 282° , yielding pyrazinecarboxylic acid, pyrazine, and carbonic anhydride. The *silver*, *calcium*, with $4H_2O$, and *barium salts* are sparingly soluble.

Pyrazinecarboxylic acid, $C_4N_2H_3 \cdot COOH$, is obtained by distilling the dicarboxylic acid; it crystallises in white prisms, sublimes when cautiously heated, and at 225° is converted into pyrazine and carbonic anhydride. The *calcium*, with $4H_2O$, and *silver salts* are well-crystallised compounds.

Pyrazine, $C_4N_2H_4$, is best obtained by slowly distilling the dicarboxylic acid. It distils at 115° under 730 mm. pressure, and solidifies in the receiver to a white, crystalline mass which melts at 55° . It crystallises in large prisms, has an odour resembling that of heliotrope or fennel, and is very like tetramethylpyrazine. It is very volatile, and sublimes at the ordinary temperature when placed in a closed vessel. The *hydrochloride*, $C_4N_2H_4 \cdot HCl$, crystallises in large needles, sublimes above 135° without melting, and is very hygroscopic. The *picrate* crystallises in yellow needles, and melts at 157° . The *gold salt*, $C_4N_2H_4 \cdot AuCl_3$, crystallises in lustrous, yellow plates, and melts at 200° . The *silver salt*, $C_4N_2H_4 \cdot AgNO_3$, crystallises in small prisms, and melts at 257° . With potassium bismuthiodide, the solution of the base in nitric acid gives a characteristic, cinnabar-red precipitate.

Pyrazine and trimethylpyrazine, when treated with sodium and alcohol, combine with 6 hydrogen atoms, and yield respectively diethylenediamine (piperazine) and tetramethylpiperazine; the latter exists in stereometric forms, of which two have been isolated in a pure state,

and a third modification obtained in small quantities, yielding a dinitroso-derivative melting at 82—86°.

α-Tetramethylpiperazine, $C_4N_2H_6Me_4 + 2H_2O$, crystallises in white needles, melts at 84° or, when anhydrous, at 46°, and boils at 171° without decomposition. The aqueous solution has a strongly alkaline reaction. The dinitroso-compound melts at 154°, the *dibenzoyl* compound at 245°.

β-Tetramethylpiperazine, $C_4N_2H_6Me_4$, is an oil which boils at 176°, and is easily soluble in water. The dinitroso-compound melts at 99°, the *dibenzoyl* compound at 173°.

Piperazine, obtained from pyrazine, is identical with diethylenediamine. The dinitroso-compound crystallises in indented leaflets, and melts at 156—158°. The *dibenzoyl* compound melts at 191°.

E. C. R.

Paradiazine Derivatives. By P. W. ABENIUS (*J. pr. Chem.* [2], 47, 183—190; compare Abstr., 1889, 134; 1890, 268, 525).—The orientation which the author adopts for the paradiazines is expressed

by the formula $R \cdot N \begin{smallmatrix} \alpha & \beta \\ \diagup & \diagdown \\ C & C \\ \diagdown & \diagup \\ \delta & \gamma \\ C & C \end{smallmatrix} N \cdot R$. Bischoff (this vol., i, 54) has ob-

tained a compound of melting point 234°, to which he ascribes the same formula as that allotted by the author to diphenyldiketoparadiazine, obtained by the action of phosphorus and hydriodic acid on diphenyl- $\alpha\gamma$ -diketodichloroparadiazine (Abstr., 1890, 525); the latter compound, however, melts above 300°.

Diorthotolyl- $\alpha\gamma$ -tetraketoparadiazine,
$$\begin{array}{c} CO \cdot CH \cdot N \cdot C_6H_4Me \\ C_6H_4Me \cdot N - CH \cdot CO \end{array}$$

[N : Me = 2 : 1], is prepared by reducing diorthotolyl- $\alpha\gamma$ -diketodichloroparadiazine with phosphorus and hydriodic acid. It crystallises in aggregates of small needles or laminae, melts at 231—232°, and dissolves in hot alcohol, benzene, acetone, and glacial acetic acid, but not in ether or water. It dissolves in fuming hydrochloric acid, and is precipitated again, undecomposed, by water. Hot concentrated alkalis decompose it with elimination of orthotoluidine and oxalic acid. It reduces ammoniacal silver oxide very easily; a reaction which it shares with all the $\alpha\gamma$ -diketoparadiazines. Attempts to displace the chlorine by hydrogen by means of nascent hydrogen proved unsuccessful.

Diorthotolyltetraketoparadiazine, $C_6H_4Me \cdot N : (CO \cdot CO)_2 \cdot N \cdot C_6H_4Me$ [N : Me = 2 : 1], is obtained by oxidising the diketoparadiazine with as little chromic acid as possible in cold glacial acetic acid (compare the behaviour of the diketodihydroparadiazine, Abstr., 1890, 525); it crystallises in lustrous needles or prisms, melts at 274°, and dissolves best in hot acetone. When heated with toluidine, it is converted into diorthotolylloxamide (m. p. 210°), which, together with oxalic acid and oxalorthotoluidic acid (m. p. of crystals, with 1 mol. H_2O , 83—84°; Abstr., 1886, 886), is also obtained when it is heated with dilute potash or soda. Oxidation by hot chromic acid converts it into diorthotolylparabanic acid.

A. G. B.

Oxidation of Azimidotoluene. By J. A. BLADIN (*Ber.*, 26, 545—546).—When azimidotoluene, $C_6H_3Me \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix}$, is carefully oxidised with alkaline potassium permanganate, the benzene nucleus is destroyed, and the substance converted into 1:2:3-*triazoledicarboxylic acid*, $N \begin{smallmatrix} \text{N}-C \cdot COOH \\ \diagup \quad \diagdown \\ \text{NH} \cdot C \cdot COOH \end{smallmatrix}$, this being the first known derivative of a triazole in which the three nitrogen atoms occupy the adjacent position. It crystallises from fuming hydrochloric acid in colourless plates or large prismatic crystals, and melts at 200° with violent evolution of gas and formation of a brown oil. It liberates carbonic anhydride from carbonates, but does not yield a nitroso-derivative. The normal salts are very soluble in water, but the acid salts crystallise well; the *acid potassium salt*, $C_4H_2N_3O_4K + H_2O$, forms colourless needles, and the *acid sodium salt*, $C_4H_2N_3O_4Na + 2H_2O$, slender needles which rapidly change into small prisms.

H. G. C.

Constitution of Nicotine. By F. BLAU (*Ber.*, 26, 323—633; compare *Abstr.*, 1892, 1365, and Pinner, *Abstr.*, 1892, 1497, and this vol., i, 286).—When nicotine is reduced with sodium and alcohol, it yields a very small quantity of ammonia, a rather small quantity of a substance which is non-volatile with steam, and an oil which is volatile with steam, and contains octohydronicotine and other bases.

Octohydronicotine hydrochloride, $C_{10}H_{22}N_2 \cdot 2HCl$, can be isolated by fractionally distilling the oil with steam and treating the several fractions with hydrochloric acid; it is a crystalline substance, melts at 201 — 202° , and is extremely soluble in water. The *platinochloride* melts at 202° with decomposition; the *aurchloride* forms sparingly soluble, yellow plates, and melts at 142° ; the *picrate* melts at about 285° . The *base*, $C_{10}H_{22}N_2$, is a colourless oil boiling at 259 — 260° (corr.). When the hydrochloride is strongly heated in a stream of hydrogen chloride, it yields a considerable quantity of a gas which has the properties of methylic chloride; nicotine hydrochloride behaves in a similar manner, a fact which shows that the base contains a methyl group in combination with nitrogen.

The constitution of octohydronicotine may be represented by the formula $C_5NH_{10} \cdot C_4H_8 \cdot NHMe$, and that of nicotine by the formula $C_5NH_4 \cdot CH_2 \cdot CH_2 \cdot CH \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{NMe} \end{smallmatrix}$ or $C_5NH_4 \cdot CH_2 \cdot CH \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{NMe} \end{smallmatrix} > CH_2$; such a constitution of nicotine would account most satisfactorily for its behaviour and also for that of the dibromocotinine and dibromocotinine described by Pinner, assuming that the two last-named compounds have a constitution analogous to that of nicotine.

F. S. K.

Trimethylxanthine Derivatives. By M. GOMBERG (*Amer. Chem. J.*, 14, 611—619).—When caffeine is boiled with iodine in chloroform solution, and the product successively heated at 140 — 150° to remove iodine, and extracted with chloroform and carbon bisulphide, a dark,

granular powder is obtained of the composition $C_8H_{10}N_4O_2I_5$, possibly a tetriodide of iodocaffeine.

The action of sodium on a mixture of an alkylic haloïd and a halogen caffeine gave no satisfactory results. Zinc ethide did not react with either chlorocaffeine or bromocaffeine in ethereal solution, but when it is heated at 160° with bromocaffeine in the absence of a third substance, a compound containing bromine is formed, but was not obtained pure enough for analysis.

When chlorocaffeine is boiled with potassium cyanide in alcoholic solution, a substance is obtained which is perhaps an amido-derivative, $C_8H_9N_4O_2 \cdot CO \cdot NH_2$, resulting from the partial hydrolysis of cyanocaffeine, $C_8H_9N_4O_2 \cdot CN$, formed in the first instance.

C. F. B.

Mercuriodides of Organic Bases. By A. B. PRESCOTT (*Amer. Chem. J.*, **14**, 606—611).—The mercuriodides of quinine, pyridine (boiling at 114.5°), and quinoline were prepared by precipitating solutions of the alkaloids at 25° with a decinormal solution of potassium mercuriodide, excess of the latter being avoided. In the case of quinine, the concentration of the solution was varied, but this had no effect on the composition of the precipitate, analyses of which agree best with the formula $2C_{20}H_{24}N_2O_2 \cdot 3HI \cdot 3HgI_2 + H_2O$. The pyridine precipitate had the composition $C_5H_5N \cdot 2HgI_2$; the quinoline one, $C_9H_7N \cdot HgI_2$.

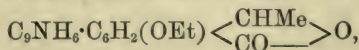
C. F. B.

Oxidation Products of Apocinchene. By W. KOENIGS (*Ber.*, **26**, 713—721).—Cinchonine and cinchonidine, when successively treated with phosphorus pentachloride and alcoholic potash, are converted into cinchene, $C_{19}H_{20}N_2$, and this base, when boiled with concentrated hydrobromic acid, yields apocinchene, $C_{19}H_{19}NO$. The author and others (*Ber.*, **14**, 1855; *Abstr.*, 1885, 1248, and 1888, 71) have already shown that, from apocinchene, an ethyl ether is obtained, which, when oxidised, yields a monocarboxylic acid, and that this, when boiled with concentrated hydrobromic acid, yields ethylic bromide, carbonic acid, and homapocinchene, $C_9NH_6 \cdot C_8H_8 \cdot OH$. Hence, the formula for apocinchene may be written $C_9NH_6 \cdot C_8H_7Et \cdot OH$.

By oxidising ethylapocinchene with lead peroxide or manganese dioxide and dilute sulphuric acid, ethylapocinchenic acid, together with the two new compounds, ketoethylapocinchene and the lactone of hydroxyethylapocinchenic acid, are produced.

Ketoethylapocinchene, $C_9NH_6 \cdot C_8H_2Et(OEt) \cdot COMe$, melts at $104-106^\circ$, and, when boiled with concentrated hydrobromic acid, is converted into homapocinchene. The *oxime* melts at $181-184^\circ$.

The lactone of hydroxyethylapocinchenic acid,



melts at $212-213^\circ$. It does not dissolve in soda, and, when boiled with alcoholic solutions of the alkalis, yields salts of the hydroxy-acid. It is also formed by boiling ethylapocinchenic acid with lead peroxide and sulphuric acid. When reduced with amorphous phosphorus and hydriodic acid, it gives a quantitative yield of homapocinchene.

When boiled with hydrobromic acid, it yields the lactone of hydroxy-apocinchenic acid, $C_9NH_6 \cdot C_6H_2(OH) < \begin{smallmatrix} CHMe \\ CO \end{smallmatrix} > O$, which melts at 274° . It is extremely stable towards oxidising agents. When converted into the alkali salt and treated with permanganate, it is slowly oxidised. When the alkali salt is treated with a solution of bromine in dilute sodium hydroxide, it yields quinolinephenetoildicarboxylic acid.

Quinolinephenetoildicarboxylic acid, $C_9NH_6 \cdot C_6H_2(OEt)(COOH)_2$, melts at $230\text{--}240^\circ$ with decomposition, gives unstable salts with mineral acids, and well-characterised metallic salts. The *anhydride* melts at $210\text{--}211^\circ$, and yields a fluorescein-like compound with resorcinol. When oxidised with chromic acid, it yields cinchoninic acid.

Ethylhomapocinchene, $C_9NH_6 \cdot C_6H_3Et \cdot OEt$, when oxidised with lead peroxide or manganese dioxide and sulphuric acid, yields cinchoninic acid, ketoethylhomapocinchene and ethylhomapocinchenic acid.

Ketoethylhomapocinchene, $C_9NH_6 \cdot C_6H_3(OEt) \cdot COMe$, melts at $107\text{--}109^\circ$. The *phenylhydrazone* melts at $218\text{--}220^\circ$. When warmed with methyl alcohol, iodine, and potassium carbonate, it yields iodoform and ethylhomapocinchenic acid. The same acid is obtained by heating the ketone with an alkaline solution of bromine.

Ethylhomapocinchenic acid, $C_9NH_6 \cdot C_6H_3(OEt) \cdot COOH$, melts at $253\text{--}254^\circ$. When boiled with hydrobromic acid, it yields homapocinchenic acid, $C_9NH_6 \cdot C_6H_3(OH) \cdot COOH$, which does not melt at 290° .

Quinolinephenetoil, $C_9NH_6 \cdot C_6H_4 \cdot OEt$, is obtained by heating the silver salt of the preceding acid at $280\text{--}290^\circ$, and melts at $80\text{--}81^\circ$. When boiled with concentrated hydrobromic acid, it yields *quinoline-phenol*. The latter melts at 208° , and dissolves in fixed alkalis and mineral acids. The *hydrochloride* melts at 260° .

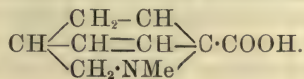
From the above results, the author deduces for apocinchene the formula $C_9NH_6 \cdot C_6H_2Et_2 \cdot OH$ [$OH : Et : Et = 1 : 2$ or $4 : 3$].

E. C. R.

Constitution of Anhydroecgonine. By A. EINHORN and Y. TAHARA (*Ber.*, 26, 324—333).—In his paper on the constitution of tropine (*Abstr.*, 1892, 360), Merlin has proposed for anhydroecgonine, which Einhorn had previously proved to be a tropidinecarboxylic

acid, the constitutional formula $CH < \begin{smallmatrix} CH_2 \text{---} CH_2 \\ CH : C(COOH) \\ CH_2 \text{---} NMe \end{smallmatrix} > CH$; the further

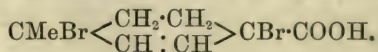
investigations described in the present paper bear out Merlin's supposition, except in the matter of the position of the carboxyl group, which, from the experiments now to be described, must be regarded as combined with one of the carbon atoms common to both the benzene and pyridine nuclei, the formula becoming



The compound which forms the starting point of the authors' researches is the *methiodide* of *anhydroecgonine ethyl ether*, which is best prepared by the action of methylic iodide on an ethereal solution of the ethyl ether, and crystallises in white plates melting at 177°. The corresponding *methochloride* is obtained from it by the action of silver chloride, and forms a hygroscopic mass, which yields a crystalline *aurochloride* and *platinochloride*.

When the aqueous solution of the methiodide is carefully treated with silver oxide, it yields a new substance, which crystallises in colourless, apparently rhombic crystals, melts with decomposition at 169°, and yields an *aurochloride*, melting at 217°. The base has the composition $C_{10}H_{15}NO_2$, and consists of *paradimethyldihydrobenzylaminecarboxylic acid*, $NMe_2 \cdot CH_2 \cdot CH < \begin{smallmatrix} CH_2 \cdot CH \\ CH : CH \end{smallmatrix} > C \cdot COOH$; it is probable that the methohydroxide is first formed, and then loses alcohol. When boiled with aqueous soda, dimethylamine is evolved, and *paramethylenehydrobenzoic acid*, $CH_2 \cdot C < \begin{smallmatrix} CH_2 \cdot CH \\ CH : CH \end{smallmatrix} > C \cdot COOH$, remains in solution. This acid may also be obtained more directly by boiling the methiodide directly with soda solution and acidifying, and forms colourless, prismatic needles, melting at 33–34°; its *silver salt* crystallises in silky plates.

Methylenehydrobenzoic acid combines readily with bromine to form a *dibromide*, $C_8H_5O_2Br_2$, which crystallises from alcohol in slender needles, and melts with decomposition at 135°. When heated with a saturated solution of hydrogen bromide in acetic acid at 100°, it combines with 2 mols. HBr , yielding *paratoluic acid dihydrobromide*, which in all probability has the constitution



It forms small, colourless crystals, melts with evolution of gas at 153°, and on boiling with aqueous soda and acidification, yields *paratoluic acid*, which was identified by its melting point and by conversion into the methyl ether and into terephthalic acid.

The formation of all these substances may be readily explained on the assumption that *anhydroecgonine* has the constitution assigned to it above; if this be correct, *ecgonine* itself must have

one of the following formulæ: $CH < \begin{smallmatrix} CH_2 \text{---} CH_2 \\ CH(OH) \cdot CH_2 \\ CH_2 \text{---} NMe \end{smallmatrix} > C \cdot COOH$,

$CH < \begin{smallmatrix} CH_2 \text{---} CH_2 \\ CH_2 \cdot CH(OH) \\ CH_2 \text{---} NMe \end{smallmatrix} > C \cdot COOH$; as no γ -lactone has yet been obtained from *ecgonine*, the authors regard the second formula as the more probable.

When *paradimethyldihydrobenzylaminecarboxylic acid* is treated with hydrogen chloride in alcoholic solution, it is converted into the *methochloride* of *anhydroecgonine ethyl ether*; this change probably takes place in three stages, the ethylic salt of the acid being first formed, and then yielding a hydrogen chloride additive product

which undergoes an intramolecular change in which the pyridine nucleus is again formed, yielding an anhydroecgonine derivative.

H. G. C.

Alkaloids of the Seeds of *Lupinus albus*. By A. SOLDIANI (*L'Orosi*, 1892, 325—348, and *Gazzetta*, 23, i, 143—168; compare *Abstr.*, 1892, 892).—The crystalline alkaloid from the seeds of *Lupinus albus*, melting at 99°, is very soluble in alcohol, ether, or chloroform, less so in benzene and light petroleum; its hydrochloride with 2H₂O melts at 105—107°, not 124° as previously stated, and is very soluble in absolute alcohol. The hydriodide melts at 179—180°, but has, probably, not yet been obtained in a state of purity; it is sparingly soluble in cold alcohol or water. The platinochloride forms red crystals soluble in water and insoluble in absolute alcohol. The aurochloride is obtained in yellow crystals melting at 182—183°.

The hydrochloride of this alkaloid is optically inactive, but the hydrochloride of the liquid isomeric alkaloid accompanying it is dextrorotatory. On purification, the liquid alkaloid may be obtained in beautiful, large crystals which are very deliquescent; the melting points of its derivatives seem to indicate its identity with lupanine from *Lupinus angustifolia*. The physiological action of the two hydrochlorides is at present under investigation. The injection of 0.005 gram of the inactive salt caused death in a frog of ordinary weight, whilst the same quantity of the active hydrochloride was not fatal.

W. J. P.

Proteids of Egg White. By RAMSDEN (*Proc. physiol. Soc.*, 1892, 23—24).—A solution of white of egg, slightly acidified in the usual manner, and kept at a temperature considerably below that of the first coagulation as ordinarily determined (57.5°), nevertheless gives in time an abundant coagulum. Repeated crops of coagulum may be obtained on keeping a solution of white of egg at the lowest "coagulation temperature." The liquid is finally almost free from proteid. A solution of Hofmeister's crystals of egg albumin, when investigated by the ordinary method of fractional heat coagulation, gives a series of coagula at temperatures almost identical with those at which coagula appear in solution of white of egg not previously freed from globulin. A solution of white of egg, freed from globulins by saturation with magnesium sulphate, gives a similar series of coagula. The ordinary method of fractional heat coagulation gives no certain indication of the presence or absence of the globulin.

W. D. H.

Behaviour of Proteids towards concentrated Hydriodic acid. By N. v. LORENZ (*Zeit. physiol. Chem.*, 17, 457—458).—In consequence of certain experiments by E. Meissl, in which he had used Zeisel's method of estimating methoxyl in connection with albuminous substances, it appeared necessary to determine, with pure proteids, whether they contain the residue O·C_nH_{2n+1} (especially O·CH₃), which is eliminated by hydriodic acid and is changed into the alkyl iodide. Distillation is carried on in a stream of carbonic anhydride with a solution in alcoholic silver nitrate, and the iodide is weighed

as silver iodide. The impure proteïds yielded silver iodide; the pure proteïds gave negative results.

W. D. H.

Crystallised Vegetable Proteïds. By T. B. OSBORNE (*Amer. Chem. J.*, 662—689).—The author has recently, or on previous occasions, prepared crystallised globulins from Brazil nuts, hemp seed, castor oil beans, flax seed, oats, and squash seeds. He now describes their properties, and gives analyses of them, comparing these with analyses made by other investigators. These globulins are all obtained by extracting the powdered seeds (previously freed from husk by sifting, and from oil by extraction with ether or light petroleum) with a warm or cold solution of sodium chloride; the filtered extract, if warm, is allowed to cool, if cold, is subjected to dialysis, in order to remove the sodium chloride. In either case, the globulin separates out, either in crystals or in spheroids, or as a mixture of both, that from hemp seed being most readily obtained crystalline. The crystals are always octahedra; sometimes they appear as hexagonal plates, but are then nothing but unequally-developed octahedra. The crystallised globulins of the Brazil nut (I) and of the oat (II) are distinct substances, for they react differently, and their composition is different, as the analyses show:—

	I.	II.	III.	IV.	V.	VI.
Carbon	52.18	52.18	51.28	51.31	51.66	51.48
Hydrogen ...	6.92	7.05	6.84	6.97	6.89	6.94
Nitrogen....	18.30	17.99	18.84	18.75	18.51	18.60
Sulphur.....	1.06	0.53	0.87	0.76	0.88	0.81
Oxygen.....	21.54	22.34	22.17	22.21	22.06	22.17
	100.00	100.00	100.00	100.00	100.00	100.00

On the other hand, the crystallised globulins of the hemp seed (III), castor oil bean (IV), squash seed (V), and flax seed (VI) are almost identical in composition, and behave in a very similar way towards reagents, those of hemp seed and castor oil beans being almost identical in the latter respect, although differing slightly from those of the squash and flax seed, which two likewise closely agree together.

C. F. B.

Tunicin. By E. WINTERSTEIN (*Ber.*, 26, 362—364).—Tunicin, purified by treatment with highly dilute acids and alkali, on hydrolysis with sulphuric acid, yields dextrose, which can be separated by means of alcohol and identified by its refractive power, the formation of the osazone and of saccharic acid, and by the action of yeast.

J. B. T.

Organic Chemistry.

Influence of Negative Groups in Organic Compounds. By T. SELIVANOFF (*J. Russ. Chem. Soc.*, **24**, 134—135).—From his experiments on halogen amines and from other data, the author concludes that when a halogen atom is attached to a carbon atom which is directly combined with other strongly negative groups, it is possessed of "active" (that is, oxidising) properties. He adduces as instances, such compounds as $\text{CX}\cdot\text{SO}_2\text{R}$, $\text{CX}(\text{SO}_2\text{R})_2$, where X is a halogen atom, and $\text{CBr}_2(\text{NO}_2)_2$, $\text{CHBr}(\text{NO}_2)_2$, $\text{CMeBr}(\text{NO}_2)_2$, and $\text{CHMe}_2\cdot\text{CBr}(\text{NO}_2)_2$. J. W.

Composition of Commercial Amylene. By I. KONDAKOFF (*J. Russ. Chem. Soc.* **24**, 92—113).—Chlorine combines with the amylene prepared from methylpropylcarbinylic iodide, yielding an amylenic chloride (560 grams from 320 grams of amylene) boiling at $139\cdot5$ — $140\cdot5^\circ$. A small quantity of a chloramylene is formed simultaneously. The amylenic chloride is identical with that produced by the addition of chlorine to symmetrical methylethylethylene. In this case, the quantity of chloramylene formed is exceedingly small. The sp. gr. of the chloride of methylethylethylene is $0\cdot0973$ at $0^\circ/0^\circ$ and $1\cdot0821$ at $20^\circ/0^\circ$.

The author studied the action of chlorine on the hydrocarbons remaining after commercial amylene had been treated with concentrated sulphuric acid. 1000 grams yielded 405 grams of isopentane, and 1120 grams of different products containing chlorine, of which 720 grams boiled at 139 — $140\cdot5^\circ$, and 280 grams at 142 — 144° . From the chief fraction, alcohols were obtained by prolonged treatment with water, and then with caustic potash. The alcoholic product was fractionated, and the separate fractions distilled with strong sulphuric acid. Amongst the products were found, methyl isopropyl ketone, methylpropylcarbinol, methylethylacetaldehyde, and isopropylacetaldehyde, but no normal valeraldehyde. From the velocity of etherification, it was shown that the mixture contained primary and secondary unsaturated alcohols, consisting, in fact, of β -dimethylallylic and α -ethylacrylic (or tiglic) alcohols, both derived from asymmetrical methylethylethylene.

The fraction of the chlorides boiling at 142 — 144° was shown to be the chloride of isopropylethylene.

The oxidation of the original mixture of hydrocarbons by potassium permanganate yielded acetaldehyde, propaldehyde, and isobutaldehyde, the corresponding acids, and also formic, oxalic, and dihydroxyvaleric acids. Neither normal butyric nor succinic acid could be detected.

From these observations, the author concludes that in commercial amylene there is no propylethylene, and that the product, after extraction with concentrated sulphuric acid, contains isopentane,

symmetrical methylethylethylene, and isopropylethylene, besides small quantities of trimethylethylene and asymmetrical methylethylethylene.
J. W.

Syntheses in the Fatty Series by means of Zinc Chloride.

By I. KONDAKOFF (*J. Russ. Chem. Soc.*, **24**, 309—317).—Trimethylethylene, if heated with zinc chloride at 70° , gives a considerable quantity of diamylene. The same hydrocarbon, when mixed with acetic acid and zinc chloride, at once forms an amylic acetate boiling at $124\text{--}135^{\circ}$. This, however, is a mixture of isomeric ethereal salts, and when treated with gaseous hydrogen chloride, yields tertiary amylic chloride and an ethereal salt boiling at $130\text{--}135^{\circ}$, probably $\text{CH}_3\cdot\text{COO}\cdot\text{CH}_2\cdot\text{CHMeEt}$, or $\text{CH}_3\cdot\text{COO}\cdot\text{CHMePr}^a$.

When trimethylchloromethane is mixed in molecular proportion with trimethylethylene and a small quantity of zinc chloride, action takes place after some hours, and is complete in the course of a day. Diamylene is formed, possibly by the addition and subsequent withdrawal of hydrogen chloride. Acetic chloride acts at once on trimethylethylene under the influence of zinc chloride, giving an unsaturated ketone, $\text{CMe}_2\cdot\text{CMe}\cdot\text{CO}\cdot\text{CH}_3$.

Isopropylethylene was not affected by remaining in contact with zinc chloride for eight months at the ordinary temperature.

The amylenes obtained from the iodide of fermentation amyl alcohol gives a double compound with zinc chloride, which is decomposed by gaseous hydrogen chloride with formation of tertiary amylic chloride, and by water with formation of dimethylethylcarbinol. On prolonged contact, or rapidly at 100° , a diamylene is produced, and pure isopropylethylene remains behind unchanged.
J. W.

Ethereal Salts of Nitrous acid. By I. BEVAD (*J. Russ. Chem. Soc.*, **24**, 125—127).—By the action of silver nitrite on isopropyl iodide, the author obtained a substance boiling at $39\text{--}39.5^{\circ}$ under a pressure of 752 mm. On treatment with fuming hydriodic acid and hydrogen sulphide solution, it was converted into isopropyl alcohol and nitric oxide. With alcoholic soda, it gave sodium nitrite and ethyl isopropyl ether. An alcoholic solution of sodium nitrite gives the precipitates with cupric sulphate, ferric chloride, and silver nitrate which have been supposed to characterise the nitro-compounds.

From these experiments, the author concludes that the substance is a true ethereal salt of nitrous acid, $\text{RO}\cdot\text{NO}$. Similar results were obtained with the products from silver nitrite and ethylic and methylic iodides.
J. W.

Action of Zinc Chloride on Fatty Alcohols. By I. KONDAKOFF (*J. Russ. Chem. Soc.*, **24**, 114—123).—From a consideration of the results obtained by various observers, the author classifies the different actions of zinc chloride on fatty alcohols as follows:—

- a. Dehydration with formation of simple ethers and olefines.
- b. Isomerisation of these olefines.

c. Formation of homologues of the olefines which have the same number of carbon atoms as the alcohols employed.

d. Polymerisation of the olefines.

e. Reduction of the olefines.

f. Etherification of the alcohols.

g. Oxidation of the alcohols (to aldehydes).

He also discusses at some length the formation of the isomeric amylenes obtained from isoamyl alcohol by means of zinc chloride.

J. W.

Action of Iodine on Sodium Propoxide. By A. KESSLER (*J. Russ. Chem. Soc.*, **24**, 299—304).—Sodium (16·5 grams) was dissolved in propyl alcohol (175 grams), and the solution cooled to 6°, when it solidified. Iodine (450 grams) was then added in small portions at a time with continual shaking. The reaction went on quietly, the alcoholate disappearing, and sodium iodide precipitating. Finally, the cooled solution was neutralised with a 10 per cent. solution of tartaric acid, and treated with enough water to precipitate the whole of the iodoform produced during the action. The aqueous liquid was then separated by distillation into fractions boiling at 89—92°, 92—100°, and 100—100·5°. Each of these was then carefully fractionated by itself. From the first portion, which consisted chiefly of a mixture of propyl alcohol and water of constant boiling point, an oil was obtained which distilled between 111° and 114° under a pressure of 26—28 mm., and, on analysis, gave numbers agreeing with the formula $C_9H_{20}O_3$. A molecular weight determination by the cryoscopic method confirmed this formula. From its behaviour towards acetic acid, on heating with which it gives propylic acetate, and what is apparently an hydroxyaldehyde, the author concludes that the substance is the dipropyl ether of α -hydroxypropaldehyde, $OPr \cdot CHMe \cdot CH(OH) \cdot OPr$.

J. W.

Action of Sodium on Epichlorhydrin. By N. KIJNER (*J. Russ. Chem. Soc.*, **24**, 31—39).—Hübner and Müller (*Annalen*, **159**, 184) found that sodium and epichlorhydrin reacted in ethereal solution with separation of sodium chloride and formation of the sodium compound of a substance b. p. 218—225°, to which they attributed the formula $C_6H_{12}O_2$. The author has repeated their experiments as follows:—Sodium (70 grams) in the granular form was covered by a layer of dry ether, and to it epichlorhydrin (100 grams) was added drop by drop, the flask being cooled with ice, and frequently shaken. A yellowish solid mass was formed, consisting of a mixture of sodium chloride and the sodium compound of an alcoholic product. After a lapse of 12 hours, the contents of the flask were treated with small quantities of dilute alcohol to destroy the excess of sodium, then with a large quantity of water, and were finally acidified with sulphuric acid. The ethereal layer was dried and the ether distilled off, when 36 grams of an oil free from chlorine remained behind; on fractionation, this yielded a small quantity of allyl alcohol, a product boiling at 225—227°, and a thick oily residue. The portion boiling at 225—227° was proved by

analysis and by the determination of the lowering of the freezing point of benzene, to have the composition $C_9H_{16}O_3$, not $C_6H_{12}O_2$, as found by Hübner and Müller. It united readily with bromine, and was reduced at 100° by hydriodic acid (sp. gr. 1.96) to isopropyl iodide. Acetic chloride gave a monacetate. From these reactions, it appeared probable that the substance was a diallyl ether of glycerol, formed by the action of sodium allyl oxide on epichlorhydrin. Experiment showed this explanation to be the correct one, allyl alcohol, sodium, and epichlorhydrin interacting very readily, with formation of a diallyl ether of glycerol. The author has not determined which of the possible isomerides is produced, nor, indeed, that the substance is not a mixture of both.

Diallyl ether of glycerol, $C_9H_{16}O_3$. B. p. $224-228^\circ$. Sp. gr. at $0^\circ/0^\circ$, 0.997; at $18^\circ/0^\circ$, 0.9824. *Acetate*, $C_9H_{15}O_3Ac$. B. p. $240-244^\circ$. Sp. gr. at $20^\circ/0^\circ$, 1.000.

The diallyl ether seems to polymerise on keeping, becoming viscous, and giving a depression of the freezing point in benzene solution nearly corresponding with a molecule double that of the ether.

J. W.

Phlorose. By E. SCHUNCK and L. MARCHLEWSKI (*Ber.*, 26, 942—943).—The authors bring forward conclusive proof of the accuracy of Rennie's results (*Trans.*, 1887, 636), that the so-called phlorose is identical with d.-glucose (dextrose).

A. R. L.

Action of Hydrogen Peroxide on Starch. By A. V. ASBÓTH (*Chem. Zeit.*, 16, 1517—1518; 1560—1561).—Lintner (*Abstr.*, 1891, 537) has studied the action of potassium permanganate, and Petit (*Abstr.*, 1892, 1171) that of nitric acid, on starch.

When a paste of potato starch (150 grams) and water (500 grams) is boiled during the addition of hydrogen peroxide (750 grams) made faintly alkaline with ammonia, liquefaction sets in at the end of a minute, and oxygen and carbonic anhydride are evolved. The yellow solution is filtered from the precipitate, which is probably starch cellulose, and the filtrate fractionated as described below. The compounds obtained are without action on Fehling's solution, but reduce silver nitrate solution, forming metallic mirrors; on being boiled with hydrochloric acid, they are readily saccharified.

The first separation is effected by pouring the last mentioned filtrate into 96.5 per cent. alcohol (3 litres); the precipitate which represents the chief part of the transformation product is kneaded with alcohol; it forms a grey, porous mass; its aqueous solution gives a bluish-violet coloration with iodine, and its specific rotatory power is $[\alpha]_D = 178^\circ$. It holds iron and copper salts in solution in the presence of alkalis, but is precipitated from its aqueous solution on the addition of either alcohol or barium hydroxide. Analysis gave values agreeing with the empirical formula $C_6H_{10}O_5 + H_2O$, and the author regards it as identical with "soluble starch" or "amylodextrin."

If the alcoholic filtrate is allowed to remain for a time, another substance, $C_{24}H_{42}O_{20} + 4H_2O$, separates, the aqueous solution of which gives a violet-red coloration with iodine. It is precipitated from its aqueous

solution by alcohol, but not by barium hydroxide, and its specific rotatory power is $[\alpha]_D = 170^\circ$.

Barium hydroxide is added to the alcoholic filtrate from the last-described compound, and the resulting precipitate is dissolved in hydrochloric acid and the barium precipitated by sulphuric acid. When purified by dissolving it in water and reprecipitating with alcohol, it forms a pulverulent mass having the composition $C_6H_8O_4 + H_2O$. It gives no coloration with iodine.

The substance remaining in the alcoholic solution after the last separation consists of a small quantity of sugar. A. R. L.

Inulin, Pseudoinulin, and Inulenin. By C. TANRET (*Compt. rend.*, 116, 514—517).—In the Jerusalem artichoke, and in elecampane, inulin is associated with two allied substances, *pseudoinulin* and *inulenin*. The three compounds are separated by means of their different solubilities in solutions of barium hydroxide.

The boiling juice of artichokes taken up in September or October is treated with lead acetate, and after cooling and separation of the lead by means of sulphuric acid, a concentrated solution of barium hydroxide is added so long as a precipitate forms, and then 20 per cent. of alcohol of 80° . The precipitate is washed with cold barium hydroxide solution, then decomposed by carbonic anhydride, and mixed with a large quantity of cold barium hydroxide solution. The precipitate obtained under these conditions is rich in inulin, but contains little of the other two compounds. The inulenin and pseudoinulin are in the mother liquor, which is mixed with successive quantities of dilute alcohol, the precipitates that form being collected and decomposed by carbonic anhydride.

The compound of inulin with baryta is repeatedly treated in the same manner until all pseudoinulin and inulenin have been removed, and it is then dissolved in hot water, decomposed by carbonic anhydride, the solution filtered, treated with animal charcoal, and mixed with alcohol of 95° . Pure inulin separates, and is washed with concentrated alcohol.

The solutions containing pseudoinulin and inulenin are evaporated to dryness, dissolved in a cold solution of pure barium hydroxide, and mixed with a further quantity of the same solution until the precipitate ceases to form. This precipitate, when decomposed by carbonic anhydride, yields pseudoinulin.

The solution is treated with carbonic anhydride, filtered, and evaporated to dryness. The residue is agitated with 10 times its weight of water, filtered after 24 hours, evaporated to dryness, and the residue treated with five or six times its weight of boiling alcohol of 30° , from which the inulenin crystallises.

Inulin deposited from water or dilute alcohol forms compact, transparent masses when dried, but if previously washed with strong alcohol, it forms a pulverulent solid resembling starch. After drying at 100° , its rotatory power is $[\alpha]_D = -38.8^\circ$, and is not affected by the temperature or concentration of the solution. Its composition agrees with Kiliani's formula, $6C_6H_{10}O_5 \cdot H_2O$, but cryometric observations indicate that this must be quintupled to represent the molecule.

With barium hydroxide, inulin forms the compound $C_{36}H_{62}O_{31}, 3BaO$. Inulin dissolves in 10,000 parts of cold water, but is readily soluble in hot water, and also in hot dilute alcohol; contrary to the usual statement, its solutions are not opalescent.

Pseudoinulin, according to analysis and cryometric observations, has the composition $16(C_6H_{10}O_5), H_2O$. With baryta in aqueous solution, it forms the compound $16(C_6H_{10}O_5), H_2O, 6BaO$, but in presence of alcohol the compound formed is $16(C_6H_{10}O_5), H_2O, 8BaO$. The calcium compound formed in presence of alcohol is analogous in composition. Basic lead acetate does not precipitate pseudoinulin, but in presence of ammonia the compound $16(C_6H_{10}O_5), H_2O, 19PbO$ is formed. Pseudoinulin resembles inulin in appearance, but dissolves in 350 to 400 parts of cold water, and is very soluble in hot water and in hot dilute alcohol. Its rotatory power is $[\alpha]_D = -32.2^\circ$, and when treated with dilute acids it becomes $[\alpha]_D = -85.6^\circ$. The mixture of sugars obtained by inversion very readily yields crystallised levulose, and also contains a dextrogyrate sugar which is probably glucose.

Inulenin when dried at 100° has the composition $10(C_6H_{10}O_5), 2H_2O$. It crystallises in slender needles, macled in pairs or arranged in stellate groups; they act on polarised light and show extinction parallel with their axes. Inulenin dried at 100° dissolves in a few parts of cold water, then becomes hydrated, and crystallises, the liquid retaining only about one-eighth of its weight of the compound. It dissolves in 35 parts of cold alcohol of 30° , and in 245 parts of alcohol of 50° . Its rotatory power is $[\alpha]_D = -29.6^\circ$, but after inversion it becomes $[\alpha]_D = -83.6^\circ$. With barium, calcium, and lead oxides, inulenin forms compounds analogous to those of inulin and pseudoinulin.

C. H. B.

Glycogen. By S. FRÄNKEL (*Pflüger's Archiv*, 52, 125—136).—A method for the preparation of glycogen in the cold is recommended, by means of which the conversion of glycogen into sugar is prevented as efficaciously as by heat. It consists in the use of dilute acids as the agents for extracting it from liver and muscle. Several acids were used, but the best results were obtained with a 2—4 per cent. solution of trichloroacetic acid. No proteid goes into solution. The glycogen is precipitated by alcohol. It gives the usual reactions of glycogen; elementary analysis gives the formula $6C_6H_{10}O_5 + H_2O$, $[\alpha]_D = 197.891^\circ$; this is a smaller value than is given by most previous observers. Doubt is expressed as to whether glycogen occurs in the body as such; water will not extract it from liver which has been hardened in alcohol; the same is true for mixtures of glycogen and albumin which have been treated with alcohol. Boiling water and the addition of small quantities of salts of the heavy metals and acids will, however, extract the glycogen.

It is regarded as probable that in the living cells a complex compound of proteid and carbohydrate exists, which may be split up by metabolic processes, or by various reagents, the carbohydrate being separated under some circumstances as glycogen, under others as sugar.

W. D. H.

Witt's Oxycellulose. By A. NASTNIKOFF (*J. Russ. Chem. Soc.*, **24**, 256—275).—The author, from experiments on the action of bleaching powder solutions on Schleicher and Schüll's filter paper, finds that no oxycellulose is formed at 19—20° if the bleaching powder solution contains less than 9.86 grams of active chlorine per litre.

The oxycellulose he obtained is turned brown by iodine, and dissolves completely in Schweitzer's reagent, from which it is again precipitated by acids. It also dissolves without residue in Cross and Bevan's solvent (zinc chloride in concentrated hydrochloric acid), the saturated solution containing about 1 gram of oxycellulose in 100 c.c. Dilution of this solution with its own volume of water brings down all the precipitate that will fall out under the circumstances. Acid sodium sulphite has no action on oxycellulose, either at the ordinary temperature or at 100°; at 140° the oxycellulose is completely destroyed. The action of moist chlorine produces no substance which gives a coloration with neutral sodium sulphite, so that if oxycellulose is, as Witt maintains, an intermediate stage between cellulose and lignin, it is much nearer the former than the latter.

The author made a large number of analyses of oxycellulose, prepared under different conditions, and comes to the conclusion that it is not a homogeneous substance. Judging from the action of phenylhydrazine, oxycellulose cannot contain more than 15 per cent. of $C_6H_{10}O_6$, supposing this to possess a carbonyl group capable of condensing with the reagent.

J. W.

Absorption of Mercuric Chloride from Dilute Solutions by Cotton. By L. VIGNON (*Compt. rend.*, **116**, 517—519 and 645—646).—Carefully purified cotton, bleached by dilute bleaching powder solution and thoroughly washed, absorbs mercury from dilute solutions of mercuric chloride, leaving the solution relatively richer in chlorine.

Part of the mercuric chloride absorbed by cotton wool is soluble in cold water, and is present in the form of unchanged mercuric salt; part is soluble in hydrochloric acid and is present as mercuric oxide, and the remainder is soluble in concentrated sodium chloride solution, and is present as mercurous chloride. At the ordinary temperature, the mercury compounds absorbed consist of 22 to 28 per cent. of mercuric chloride, 59 to 70 per cent. of the oxide, and 8 to 13 per cent. of mercurous chloride. If the cotton, after immersion, is kept for 20 days at the ordinary temperature, and then heated at 60° for 10 hours, it contains 12 to 22 per cent. of mercuric chloride, 25 to 57 per cent. of the oxide, and 22 to 53 per cent. of mercurous chloride. It is probable that the mercurous chloride is formed by the interaction of mercuric chloride and mercuric oxide, thus: $HgCl_2 + HgO = Hg_2Cl_2 + O$, the oxygen combining with the cellulose to form oxycellulose.

C. H. B.

Dimorphism of Dimethylamine Platinochloride. By LE BEL (*Compt. rend.*, **116**, 513—514).—When a solution containing di-

methylamine and diisobutylamine platinochlorides is allowed to crystallise, no double platinochloride is formed, but the dimethylamine platinochloride separates in the form of yellowish, rhombic needles with a characteristic angle of $48^{\circ} 20'$, quite different in appearance from the ordinary crystals. This dimorphic form was described by Vincent, but the conditions under which it is produced were not determined. It is this form, and not the ordinary form, of the salt that resembles the rhombic crystals of the platinochlorides of the other diamines.

The sp. gr. of the ordinary crystals is 2.27, that of the rhombic crystals 2.12. The rhombic crystals, as Vincent observed, are stable at 100° when dry, but they reproduce the ordinary form on recrystallisation. A certain number of the rhombic crystals are, however, always found, even when the salt has been dissolved in hot water, and hence it would seem that the crystalline type is conserved even in solution. This view is confirmed by the fact that the rhombic crystals are obtained by keeping a pure solution of the dimethylamine platinochloride below 0° for some time. It would seem that 10° is the critical temperature, above which there is a tendency to return to the ordinary form. At the same time, a solution that has been exposed to a low temperature for a long time, and is then heated at 30° , yields rhombic crystals during the first eight days, and afterwards the ordinary crystals. The rhombic form can be reproduced by adding cubic crystals of trimethylamine platinochloride, and, although the change is slow, the crystals obtained are large, and it is observed that the change of form is preceded by the formation of macles.

C. H. B.

Haloid Substitution Products of Amides. By T. SELIVANOFF (*J. Russ. Chem. Soc.*, **24**, 132—134; compare this vol., i, 192 and 305).—The author regards the halogen substitution products of ammonia and the amides as being amides of hypochlorous, hypobromous, and hypiodous acids, for in presence of water they give the reactions of these acids. For each atom of chlorine in a chloramido-compound 2 atoms of iodine are liberated from a solution of potassium iodide on acidification.

By making use of the following reaction between amines and haloid substituted amides, $\text{RNH}_2 + 2\text{CH}_3\cdot\text{CO}\cdot\text{NHBBr} = \text{RNBBr}_2 + 2\text{CH}_3\cdot\text{CO}\cdot\text{NH}_2$, the author has succeeded in preparing a whole series of bromamines, &c.

Acetiodamide, $\text{CH}_3\cdot\text{CO}\cdot\text{NHI}$, was prepared by the action of iodine on the mercury or silver compound of acetamide. It is easily decomposed by water, giving hypiodous acid, HIO , which is unstable, being at once converted into iodine and iodic acid according to the equation $5\text{HIO} = 2\text{I}_2 + \text{HIO}_3 + 2\text{H}_2\text{O}$. A similar decomposition was observed in the case of succiniodimide, $\text{C}_2\text{H}_4\langle\text{CO}\rangle\text{NI}$.

It has been stated that chloride of nitrogen is decomposed by water into nitrous acid and hydrochloric acid, but the author finds that this is not the case, hypochlorous acid being the product of the reaction.

J. W.

Nitrosoguanidine. By J. THIELE (*Annalen*, **273**, 133—144).—*Nitrosoguanidine*, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{NO}$, is formed as an intermediate product in the reduction of nitroguanidine to amidoguanidine (Abstr., 1892, 1295); on carefully treating the nitro-compound with zinc-dust and sulphuric acid and recrystallising the product from hot water, nitrosoguanidine is deposited in slender, yellow needles. It explodes rather violently at $160\text{--}165^\circ$, and is insoluble in alcohol, but dissolves in alkalis, being reprecipitated from the solution by carbonic acid; it is readily soluble in dilute mineral acids, the solutions undergoing decomposition, even at the ordinary temperature, with evolution of nitrous acid and formation of guanidine. It gives Liebermann's reaction, and decomposes suddenly when treated with concentrated sulphuric acid; its alkaline solutions give, with ferric salts, a beautiful, purple coloration which disappears when the solution is exposed to the air or treated with oxidising agents. When boiled with water, it is decomposed into nitrogen, cyanamide, and water; on oxidation, it gives nitroguanidine, and, on reduction, amidoguanidine. The *hydrochloride*, $\text{CH}_3\text{N}_4\text{O}\cdot\text{HCl}$, is a yellow powder, readily soluble in alcohol; it is decomposed by water, and is extremely unstable in the dry state, exploding sometimes at ordinary temperatures. The *silver* derivative, $\text{CH}_3\text{N}_4\text{OAg}$, is a colourless, flocculent, explosive substance, and is readily soluble in acids. The *copper* derivative, $(\text{CH}_3\text{N}_4\text{O})_2\text{Cu}$, is a reddish-brown, the *nickel* derivative, $(\text{CH}_3\text{N}_4\text{O})_2\text{Ni}$, a vermilion substance.

When nitrosoguanidine is treated with an equivalent quantity of hydrazine hydrate, it is converted into amidoguanidine with evolution of nitrogen; when, however, 2 molecular proportions of the nitroso-compound are employed to 1 of the hydrate, hydrazodicarbonamidine (*loc. cit.*) is formed.

F. S. K.

Formaldehyde. By G. PULVERMACHER (*Ber.*, **26**, 955—958).—Methylenediorthonitraniline (Abstr., 1892, 1450) is readily prepared by adding a solution of formaldehyde to one of orthonitraniline in boiling 5—10 per cent. alcohol. On reduction, the three isomerides (*loc. cit.*) yield the corresponding phenylenediamines.

Methylenephthalamide acid, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}\cdot\text{CH}_2$, is obtained by heating together phthalamide and formaldehyde in a sealed tube at 100° ; it crystallises in prisms, melts at 144° , is almost insoluble in water, and is hydrolysed into formaldehyde and phthalamide when boiled with that liquid. The *silver* salt is a white powder, which is not altered by exposure to light. When a mixture of formaldehyde and oxamide is heated at 130° , ammonium oxalate is formed.

A. R. L.

Condensation of Chloral with Ketones. By J. WISLICENUS, T. KIRCHEISEN, and E. SATTLER (*Ber.*, **26**, 908—915).—The authors have unknowingly been working in the same direction as Koenigs (Abstr., 1892, 694; and this vol., i, 302).

When a mixture of chloral and acetone is heated in a sealed tube at 100° , and then at 150° , a mixture of trichlorethylideneacetone, $\text{CCl}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe}$, and chloralacetone, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{COMe}$, is

obtained. The former is separated by distillation with steam; it boils at 136—140° under 120 mm. pressure.

Chloralacetone has the properties assigned to it by Koenigs. The oxime crystallises in beautiful, radiating needles, and melts at 104—106° (Koenigs gives m. p. 95—105°). When the lactone is warmed with sodium hydroxide or carbonate, large quantities of resin are formed, together with formic and acetic acids, and a crystalline acid, which the authors believe to be β -acetylacrylic acid. *Dibromochloralacetone* crystallises in colourless, silky needles, and melts at 117—118°.

Chloralacetophenone has the properties assigned to it by Koenigs. It melts at 76°. The oxime melts at 131—132°. The hydrazone melts at 141—142°. When treated with bromine in carbon bisulphide solution, it yields one monobromo-derivative, and not two as stated by Koenigs, who used chloroform as the solvent; this crystallises in colourless, lustrous prisms, and melts at 97°.

Trichlorethylideneacetophenone is most easily obtained by warming chloralacetophenone with phosphoric anhydride. It crystallises from alcohol in leaflets, from carbon bisulphide in thin, rhombic tablets, and from light petroleum in glassy prisms, and melts at 100°. By prolonged treatment at the ordinary temperature with water acidified with hydrochloric acid, and more quickly at 140°, it is converted into chloralacetophenone. The *oxime* crystallises from nitrobenzene in white needles, and melts at 300° with decomposition. The *dibromo-derivative*, $\text{CCl}_3\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{COPh}$, crystallises in tablets, and melts at 65—66°.

When chloralacetophenone is mixed with sodium carbonate and the mixture subjected to steam distillation, it yields chloroform, acetophenone, benzoic acid, formic acid, and a non-volatile acid, which the authors believe to be *diphenacylacetic acid*, $\text{COOH}\cdot\text{CH}(\text{CH}_2\cdot\text{CPhO})_2$. The latter crystallises in silky needles, and melts at 131—132°.

The following salts are described: *Sodium salt*, *calcium salt*, $\text{C}_{30}\text{H}_{30}\text{O}_8\text{Ca} + 6\text{H}_2\text{O}$; *barium salt*, $\text{C}_{30}\text{H}_{30}\text{O}_8\text{Ba} + 6\text{H}_2\text{O}$; *silver salt*, $\text{C}_{18}\text{H}_{15}\text{O}_4\text{Ag}$. The *ethylic salt* crystallises in long, silky needles, and melts at 64°.

E. C. R.

Pinacone from Ethyl Methyl Ketone. By N. ZELINSKY and S. KRAPIVIN (*J. Russ. Chem. Soc.*, **24**, 24—26).—Ethyl methyl ketone was prepared from diethylic methylacetoacetate, and reduced according to the directions given by Lavrinovitch (*J. Russ. Chem. Soc.*, **7**, 235; **8**, 338). In this way an oil was obtained, which was distilled, and collected in three fractions, namely, below 200°, at 200—205°, and at 205—210°. The first fraction was liquid, the second and third partially solid. After remaining for a long time in a desiccator, the solid was separated from the oily liquid and recrystallised from ether. It then melted at 49·5°, and had the composition of the pinacone, $\text{OH}\cdot\text{CMeEt}\cdot\text{CMeEt}\cdot\text{OH}$. The oil in the fraction 200—205° had the same composition. There are, probably, therefore two geometrically isomeric pinacones formed by the reduction, the formula given above containing two similar asymmetric carbon atoms.

J. W.

Action of Potassium Carbonate on Dichloroketones. By A. E. FAVORSKY (*J. Russ. Chem. Soc.*, **24**, 254—255).—The dichloroketone, $\text{CH}_2\text{Me}\cdot\text{CCl}_2\cdot\text{COMe}$, obtained by the addition of hypochlorous acid to methylethylacetylene, was heated with a 10 per cent. solution of potassium carbonate. Amongst the products of the reaction the following substances were found. The tetramethylquinone of Nef and Pechmann, which crystallised in characteristic, yellow needles and melted at 111° ; a liquid acid boiling at $181\text{--}183^\circ$, the calcium salt of which gave on analysis numbers corresponding with the formula $\text{Ca}(\text{C}_5\text{H}_7\text{O}_2)_2$; and a solid acid melting at 45° , probably angelic acid. The author conceives the reaction to take place as follows: First, the dichloroketone is converted by the carbonate into a diketone, which under the influence of the alkali is converted, on the one hand, into tetramethylquinone, and, on the other, combines with a molecule of water, and, like benzile, undergoes isomeric transformation into a hydroxy-acid, in this case methylethylglycollic; the latter, under the conditions of its formation, at once splits up into water and two unsaturated acids—angelic and ethylacrylic. J. W.

Action of Iodine on the Silver Salts of Fatty Acids. By A. SIMONINI (*Monatsh.*, **14**, 81—92).—The author has previously shown (compare Abstr., 1892, 1301) that, by the action of iodine on the silver salts of acetic and caproic acids, at a temperature slightly above 100° , methylic acetate and amylic caproate, respectively, are formed. He has recently extended his investigations to the silver salts of butyric and palmitic acids, which under similar conditions, yield propylic butyrate and pentadecylic palmitate respectively, and finds that the reaction takes place in two phases. At the ordinary temperature silver iodide separates, but the alkylic salts named above are not formed until a temperature of about 100° is reached.

When a mixture of iodine and silver caproate is heated to a temperature slightly below 50° , and the product is exhausted with light petroleum, a peculiar compound, which contains iodine, silver, and the acid radicle, is obtained. It is very unstable, and is readily decomposed by water, giving silver iodide (2 mols.), silver iodate (1 mol.), and the free acid (6 mols.), and, therefore, resembles the salts of hypiodous acid, which are not known in the free state, but appear to be decomposed by water, forming 2 mols. of iodide to each mol. of iodate. It, consequently, is best represented by the formula $\text{C}_6\text{H}_{11}\cdot\text{COO}\cdot\text{I}'''(\text{OAg})\cdot\text{CO}\cdot\text{C}_6\text{H}_{11}$. The formula explains its resolution, on heating, into amylic caproate, carbonic anhydride, and silver iodide, and the fact that, when reduced in petroleum solution with ordinary phosphorus, it gives a mixture of silver iodide and the anhydride of the acid. G. T. M.

Oximidoacetic acid. By P. P. RUBTZOFF (*J. Russ. Chem. Soc.*, **24**, 247—248).—Potassium glyoxylate (1 mol.), hydroxylamine hydrochloride (1.5 mol.), and potassium hydroxide (1.25 mol.) are dissolved in water, and the aqueous solution allowed to remain for a long time at the ordinary temperature; on subsequent acidification

with hydrochloric acid and frequent extraction with ether, a white, crystalline mass is obtained soluble in water, and melting at 127—130°. On fusion, however, it decomposes with evolution of hydrocyanic acid. On analysis, numbers were obtained agreeing approximately with the formula $C_2H_3NO_3$, the substance being in all probability oximidoacetic acid, $NOH:CH:COOH$. The yield was 21 per cent. of that theoretically possible. A larger proportion may be obtained by using dibrom- or dichlor-acetic acid and excess of potash instead of glyoxylic acid. J. W.

Amides of Hypiodous acid. By T. SELIVANOFF (*Ber.*, 26, 985—989).—Iodyl succinimide, $C_2H_4<\overset{CO}{\underset{CO}{\text{O}}}>NI$, was prepared by the author by acting on mercury succinimide with iodine in pure dry ethylic acetate. The solution in water has bleaching properties, iodises acetanilide, liberates iodine from potassium iodide solution and oxygen from barium peroxide. It behaves, in fact, potentially as a solution of succinimide and hypiodous acid. If a large excess of succinimide is added, the solution becomes much more stable and can be boiled without undergoing decomposition.

Iodyl acetamide, $CH_3\cdot CO\cdot NHI$, is much less stable than iodyl succinimide, but a colourless, aqueous solution of it may be obtained. J. W.

Presence of Linoleïc acid in some Animal Fats. By D. KURBATOFF (*J. Russ. Chem. Soc.*, 24, 26—31).—From the increase in weight of certain animal fats by oxidation in the air, the author suspected the presence in them of an acid less saturated than oleïc acid. He therefore subjected to oxidation the acids obtained from these fats by means of potassium permanganate in alkaline solution, and investigated the hydroxy-acids produced. From 29 grams of acid from the fat of the white hare he obtained 10 grams of dihydroxystearic acid (m. p. 130—134°) and 1 gram of an acid soluble in boiling water, and melting at 157—161°. From an investigation of its salts, this acid proved to be a monobasic acid having the composition $C_{18}H_{36}O_6$, being, in fact, a tetrahydroxystearic acid formed from an acid $C_{18}H_{32}O_2$ (probably linoleïc acid) present in the original substance. The same tetrahydroxy-acid was obtained from the fat of the grey hare, the Caspian seal, the silurus, and the sturgeon, although in only very small quantity from the fish. J. W.

Propylideneacetic acid and Ethylidenepropionic acid. By A. VIEFHAUS (*Ber.*, 26, 915—922).—A mixture of propylideneacetic acid and ethylidenepropionic acid is obtained by heating a mixture of malonic acid, propaldehyde, and acetic acid on the water-bath. According to Ott (*Abstr.*, 1891, 1453), the barium salt obtained from this mixture, which is crystalline and sparingly soluble in alcohol, is barium propylideneacetate, whilst the amorphous soluble salt is barium ethylidenepropionate. The author arrives at exactly the opposite conclusion.

The two acids were separated as described by Ott. The acid obtained from the crystalline barium salt boils at 120—121° under

62·5 mm. pressure, and when oxidised with potassium permanganate or nitric acid, yields oxalic and acetic acids. It is, therefore, ethylidenepropionic acid.

The acid from the amorphous barium salt boils at 126—127° under 62·5 mm. pressure, and on oxidation yields oxalic and propionic acids, and is therefore propyldieneacetic acid.

Both acids, when boiled in a reflux apparatus with sulphuric acid, diluted with an equal volume of water, yield valerolactone. Ethylidenepropionic acid is, however, more easily converted into the lactone than propyldieneacetic acid.

E. C. R.

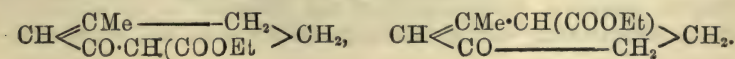
Action of Sulphuric acid on Behenolic acid. By A. HOLT and J. BARUCH (*Ber.*, 26, 838—842).—When behenolic acid is dissolved in concentrated sulphuric acid, it becomes oxidised to *oxybrassicidic acid*, $O < \begin{smallmatrix} C \cdot C_{19}H_{39} \\ | \\ C \cdot COOH \end{smallmatrix}$, which crystallises in white plates melting at 83°,

and yields a white *silver salt*, $C_{22}H_{39}O_3Ag$, stable in light. Treated with gaseous hydrogen chloride in alcoholic solution, this acid yields *ethylic dihydroxybrassicidate*, $C_{19}H_{39} \cdot C(OH) : C(OH) \cdot COOEt$, which forms colourless plates melting at 54°, and, like oxybrassicidic acid, does not take up bromine, and yields no acetyl or benzoyl derivative. With phenylhydrazine at 150°, oxybrassicidic acid yields a *phenylhydrazide*, $C_{21}H_{39}O \cdot CON_2H_2Ph$, melting at 111°, and with hydroxylamine in alcoholic soda, an *oxime*, $NOH : C_{21}H_{39} \cdot COOH$, melting at 44—45°, the *ethylic salt* of which, $NOH : C_{21}H_{39} \cdot COOEt$, melts at 28—29°. When warmed with strong sulphuric acid, this oxime is transformed into an isomeric substance, $C_{21}H_{40}NO \cdot COOH$, melting at 84—85°; the *ethylic salt*, $C_{21}H_{40}NO \cdot COOEt$, melts at 54°.

C. F. B.

Action of Methylene Iodide on Ethylic Acetoacetate. By C. T. L. HAGEMANN (*Ber.*, 26, 876—890).—When methylenic iodide is heated with an alcoholic solution of ethylic sodacetoacetate, it combines with it to form a colourless oil, which has the composition $C_{10}H_{14}O_3$; this is, however, a mixture of two isomerides, which may be separated by treating the ethereal solution with aqueous soda, which dissolves one of the compounds. The soluble oil boils at 150—152° under 22 mm. pressure, and gives a red coloration with ferric chloride, whilst the insoluble oil boils at 148—152° under the same pressure, and gives no coloration with ferric chloride.

The first product of the reaction is, in all probability, ethylic diacetylglutarate, $CH_2[CH(COOEt) \cdot COMe]_2$; in presence of sodium ethoxide, the methyl group and the carbonyl group at the opposite end of the chain act on one another with elimination of water and formation of the compound $CH < \begin{smallmatrix} CMe \cdot CH(COOEt) \\ | \\ CO - CH(COOEt) \end{smallmatrix} > CH_2$; the latter then undergoes partial hydrolysis with simultaneous evolution of carbonic anhydride, yielding, according as one or other of the $COOEt$ groups is eliminated, the two isomeric substances $C_{10}H_{14}O_3$, which have the following constitutional formulæ:—



As the compound soluble in alkali gives the colour reaction with ferric chloride characteristic of β -ketonic ethers, it has probably the first of the above formulæ.

By careful hydrolysis, both of the ethylic salts may be converted into the corresponding acids, which are extremely unstable, losing carbonic anhydride very readily, and could not therefore be closely examined. Both ethylic salts, when boiled with dilute sulphuric acid, lose the second COOEt group, forming one and the same compound, $C_7H_{10}O$, which is a mobile liquid having a pleasant characteristic odour; it boils at $200-201^\circ$ (corr.), has a sp. gr. of 0.9714 at $20^\circ/4^\circ$, and is soluble in water and the usual organic solvents. If the suppositions given above are correct, it must be 3-methyl- Δ_2 -ketoheptenylene, $CH \llcorner \begin{smallmatrix} CMe \cdot CH_2 \\ CO - CH_2 \end{smallmatrix} \gg CH_2$. This is confirmed by the fact that it unites with sodium hydrogen sulphite, phenylhydrazine, and hydroxylamine, the *oxime*, $C_7H_{10} \cdot NOH$, forming lustrous prisms, and melting at $158-159^\circ$, and that on oxidation with alkaline permanganate it yields γ -acetobutyric acid; chromic acid converts it into acetic and succinic acids and a substance which is possibly toluquinone.

The above reactions might also be explained if the substance $C_7H_{10}O$ had the constitution $COMe \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C \cdot CH$, which would be obtained if, in the formation of the anhydrides from ethylic diacetylglutarate, the methyl group had reacted with the carbonyl group adjacent to it; such a compound would, however, show the properties of an acetylene derivative, which is not the case with the substances above described.

H. G. C.

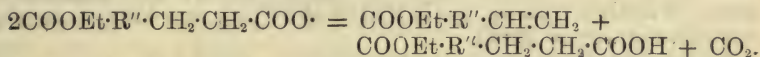
Electrolytic Synthesis of Bibasic Acids. Part II. By A. CRUM BROWN and J. WALKER (*Annalen*, **274**, 41—71; also *Trans. Roy. Soc. Edin.*, **37**, 361—379; compare Abstr., 1891, 1192, 1193).—After describing the electrolytic formation of the diethylic salts of the isomeric dimethylsuccinic and diethylsuccinic acids (Abstr., 1891, 1193), the authors proceed to the preparation and electrolysis of ethylic potassium dimethylmalonate. This salt is much more difficult to prepare than those already dealt with, which may all be obtained directly by half-saponification of the corresponding diethylic salt. Under the same conditions, diethylic dimethylmalonate is converted by the calculated quantity of alcoholic potash into a mixture of dipotassic dimethylmalonate and unchanged diethylic salt. By working at 0° , however, and using very dilute alcoholic solutions, 8 grams of potash being contained together with the methylic salt in 1750 c.c. of 95 per cent. alcohol, the ethylic potassium salt may be produced.

On electrolysis, an oil was obtained about two-thirds of which distilled above 200° , the greater part boiling between 240° and 250° ; this fraction, when hydrolysed with hydrobromic acid (sp. gr. 1.7), yielded *tetramethylsuccinic acid*, m. p. 195° . The anhydride melted at $147-148^\circ$, and the dissociation constant of the acid was found to be $K = 0.0311$.

Ethylic potassium diethylmalonate was prepared in the same way as the corresponding salt of dimethylmalonic acid, and, on electro-

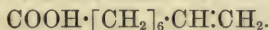
lysis, yielded an oil which boiled for the most part below 230°. The residue was fractionated at 12 mm. and gave a fraction boiling constant at 170°. This liquid was not diethylic tetrethylsuccinate, as might have been expected, but had the composition $C_{14}H_{26}O_4$. It was neutral, scarcely attacked by alcoholic potash, and had the sp. gr. 1.0082 at 13.5°/4°. A solid substance was obtained from it by heating at 110° with fuming hydrobromic acid. This was also neutral, and not appreciably attacked by any of the ordinary hydrolysing agents. It crystallised in longish, monosymmetric prisms ($a : b : c = 0.8811 : 1 : 0.9084$; $\beta = 84^\circ 27'$), melting at 84.5°, and soluble in ether, alcohol, and benzene, insoluble in water, sparingly soluble in cold light petroleum, but fairly soluble in the hot solvent.

Together with the synthetical ethereal salts produced by the electrolysis of ethylic potassium salts, there are always formed larger or smaller quantities of oils of lower boiling point; these consist chiefly of the ethylic salts of unsaturated monobasic acids. Their formation occurs according to the equation



Thus ethylic methylacrylate is produced from ethylic potassium dimethylmalonate, and ethylic ethylcrotonate from the corresponding diethylmalonate. The formation of unsaturated ethereal salts takes place much more readily with branched than with normal bibasic acids.

Ethylic potassium sebate, besides yielding the diethylic salt of *n*-dicarbodecahexanic acid, gives small quantities of the ethylic salt of an unsaturated acid, $C_9H_{16}O_2$, which has the formula



During the electrolysis, comparatively large quantities of diethylic sebate are regenerated.

The authors find that no synthetical product is obtained when the potassium ethylic salts of bromo-, hydroxy-, unsaturated, or aromatic acids are submitted to electrolysis. In their case, complete destruction of the molecule usually takes place at the anode. Potassium ethylic oxalate (prepared by boiling potassium acetate and diethylic oxalate in molecular proportions with ethyl alcohol, and filtering when cold) yields at the anode only carbonic anhydride and ethylene. Potassium methylic oxalate gives nearly pure carbonic anhydride.

J. W.

Decomposition of Solutions of Oxalic acid. By T. GIGLI (*Chem. Centr.*, 1893, i, 11; from *Apoth. Zeit.*, 7, 583—584).—The author draws the following conclusions from his experiments:—(1.) The decomposition of aqueous solutions of oxalic acid is caused by fungi or by direct exposure to light. (2.) Diffused light is most favourable to the growth of moulds. (3.) The most rapid decomposition is caused by the direct action of light. (4.) It seems probable that a decomposing action cannot be ascribed to oxygen. (5.) The carbonic anhydride that must be supposed to be formed is probably used up by the fungi, or, in decomposition by direct sunlight, is lost by diffusion; possibly, however, the decomposition of the

oxalic acid may be a reduction in which the products are carbonic oxide, oxygen, and water. A. J. G.

Derivatives of β -Methyladipic acid. By F. W. SEMMLER (*Ber.*, 26, 774—776; compare this vol., i, 129).— β -Methyladipic chloride, $\text{COCl}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COCl}$, is prepared by the action of phosphoric chloride on β -methyladipic acid, and boils without decomposition at 117—119° under a pressure of 10 mm.; its sp. gr. is 1.2201 at 20°, $n_D = 1.4709$, the molecular refractive power = 45.08. The amide, $\text{C}_7\text{H}_{10}\text{O}_2(\text{NH}_2)_2$, is deposited from water in colourless crystals which melt at 191°. Like the chloride, the amide is dextrogyrate.

The preparation of β -methylpentamethylenol, $\begin{array}{c} \text{CHMe}\cdot\text{CH}_2 \\ | \\ \text{CH}_2-\text{CH}_2 \end{array} > \text{CH}\cdot\text{OH}$, from the corresponding amine by means of the diazo-reaction has been previously described (*loc. cit.*); it is more readily obtained by the reduction of β -methylketopentamethylene in alcoholic solution by means of sodium; its sp. gr. is 0.9169 at 20°, $n_D = 1.4521$, molecular refractive power = 29.40.

By varying the experimental conditions slightly, the ketone also yields an oily reduction product, which boils at about 244° and appears to be a pinacolone.

On heating β -methylpentamethylenol at about 120° with its own weight of zinc chloride, α -methylpentamethylenylene, $\begin{array}{c} \text{CHMe}\cdot\text{CH} \\ | \\ \text{CH}_2-\text{CH}_2 \end{array} > \text{CH}$, is formed; it is a colourless oil with an odour like that of allylic sulphide, and boils at 69—71° under the ordinary atmospheric pressure; its sp. gr. is 0.7851 at 20°, $n_D = 1.4201$, molecular refractive power = 26.91. The hydrocarbon is dextrogyrate, and its constitution is proved by the fact that, on oxidation with potassium permanganate, it yields α -methylglutaric acid. J. B. T.

Condensation of Cyanides with Ethereal Salts by means of Sodium Ethoxide. By H. FLEISCHHAUER (*J. pr. Chem.* [2], 47, 375—393; compare Abstr., 1892, 431).—Ethylic sodiocyanopyruvate, $\text{CN}\cdot\text{CHNa}\cdot\text{CO}\cdot\text{COOEt}$, is a crystalline mass obtained by the action of sodium ethoxide on methylic cyanide and ethylic oxalate. The silver derivative was analysed, but attempts to isolate ethylic cyanopyruvate failed. The oxime and hydrazone (m. p. 103°) have been already described (Abstr., 1892, 431); the latter dissolves readily in acetic anhydride, and if heated therewith undergoes an isomeric change, being converted into a crystalline mass which melts at 128°.

When ethylic sodium cyanopyruvate is treated with diazobenzene chloride, the compound $\text{CN}\cdot\text{CH}(\text{N}_2\text{Ph})\cdot\text{CO}\cdot\text{COOEt}$ crystallises out; it forms yellowish-red prisms, melts with decomposition at 149°, and dissolves easily in alcohol, ether, and alkalis, but not in water. Its ammoniacal solution gives an orange-red precipitate with silver nitrate, an orange-yellow precipitate with lead acetate, and a yellowish-white one with mercuric chloride.

Attempts to produce condensation products of the homologues of methylic cyanide with ethylic oxalate proved unsuccessful, and in the paper a theoretical explanation of the failure is offered.

Methylic cyanide does not condense with ethylic succinate under the influence of sodium ethoxide, but benzylic cyanide does, producing the compound $C_2H_4(CO \cdot CHPh \cdot CN)_2$, which melts at 156° , and is soluble in alkalis.

The condensation of ethylic oxalate with dimolecular methyl cyanide in the presence of sodium ethoxide produces *ethoxalyldiacetonitrile*, $CN \cdot CH_2 \cdot CMe \cdot N \cdot CO \cdot COOEt$; this melts at 93° , and dissolves in the usual solvents, including alkalis and hydrochloric acid; when dissolved in absolute alcohol and treated with alcoholic ammonia, the *amide*, $CN \cdot CH_2 \cdot CMe \cdot N \cdot CO \cdot CONH_2$, is obtained as a white, crystalline powder which melts at 80° , and is insoluble in alcohol and water.

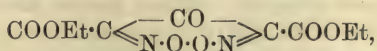
A. G. B.

Di-iodides of Tetrolic and Acetylenedicarboxylic acids. By P. BRUCK (*Ber.*, **26**, 843—848).—Tetrolic acid, like all unsaturated acids containing a triple bond, and unlike those containing a double bond, unites readily with iodine, best in chloroform solution at 100° . *Di-iodocrotonic acid*, $CMeI \cdot CI \cdot COOH$, thus obtained, forms colourless needles melting at 125° , and very sensitive to light; the *silver salt*, $C_3H_3I_2 \cdot COOAg$, crystallises in plates with a silky lustre, and is not so sensitive. The *ethylic salt*, $C_3H_3I_2 \cdot COOEt$, is a colourless oil which decomposes when boiled; the *amide*, $C_3H_3I_2 \cdot CONH_2$, forms lustrous, white needles, and melts with decomposition at 175 — 176° . When heated with water, the acid yields tri-iodopropylene, $CMeI \cdot CI_2$, acetone, and carbonic anhydride; the silver salt, when allowed to remain in contact with water, decomposes into iodallylene, $CMe \cdot CI$, carbonic anhydride, and silver iodide.

The di-iodide of acetylenedicarboxylic acid (*Abstr.*, 1892, 431) appears to be *di-iodofumaric acid*, although formed by direct addition, for it gives none of the reactions of a maleinoid compound. The *methylic salt*, $C_2I_2(COOMe)_2$, crystallises in brilliant, colourless needles melting at 126° ; the *ethylic salt*, $C_2I_2(COOEt)_2$, resembles it, and melts at 88.5° ; the *phenylic salt*, $C_2I_2(COOPh)_2$, forms needles melting at 127° ; the *chloride*, $C_2I_2(COCl)_2$, long, oblique-angled plates melting at 49° ; the *amide*, $C_2I_2(CONH_2)_2$, a colourless, amorphous powder decomposing at 210° ; the *anilide*, $C_2I_2(CONHPh)_2$, small needles decomposing at 230° . The silver salt, when boiled with water, breaks up into silver iodide, carbonic anhydride, and formic acid, the oxygen of the air taking part in the reaction.

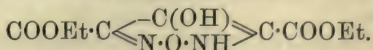
C. F. B.

Action of Nitrous acid on Ethylic Acetonedicarboxylate. By P. HENRY and H. V. PECHMANN (*Ber.*, **26**, 997—1008).—In addition to the substances previously obtained (*Abstr.*, 1887, 28; 1891, 738), *ethylic dinitrosoacetonecarboxylate peroxide*,



has been got from ethylic acetonedicarboxylate (*Abstr.*, 1891, 671)

by adding the latter to a cooled solution of nitrous anhydride in strong nitric acid. It forms yellow plates melting at 117—118°, and is fairly stable towards acids, but is decomposed by dilute alkalis into nitrous acid and ethylic hydroxyisoxazoledicarboxylate (Abstr., 1891, 738). When reduced, best with sodium hydrogen sulphite, it yields *ethylic hydroxyazoxazinedicarboxylate*,

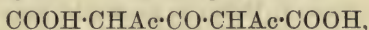


This forms white, silky needles melting at 169°, gives, like a phenol, a violet colour with ferric chloride, and reacts as a monobasic acid when titrated with an alkali, but yet contains two replaceable hydrogen atoms, as the sequel shows. It yields an *acetyl derivative*, $\text{OH} \cdot \text{C}_3\text{ON}_2\text{Ac}(\text{COOEt})_2$, as silky needles melting at 93°. When its silver salt is warmed with an ethereal solution of ethylic iodide, there is obtained an *ethyl derivative*, $\text{OH} \cdot \text{C}_3\text{ON}_2\text{Et}(\text{COOEt})_2$, melting at 74°, which reacts as a monobasic acid, and, when treated with benzoic chloride in the presence of soda, yields an *ethylbenzoyl derivative*, $\text{OBz} \cdot \text{C}_3\text{ON}_2\text{Et}(\text{COOEt})_2$, as colourless needles melting at 69°; the last compound no longer gives a colour reaction with ferric chloride, unlike the preceding ones, which still contain a C(OH) group. When the silver salt of the ethyl derivative is treated with ethylic iodide, a *diethyl derivative*, $\text{OEt} \cdot \text{C}_3\text{ON}_2\text{Et}(\text{COOEt})_2$, is obtained as needles melting at 72°, and giving no colour reaction with ferric chloride; by hydrolysis with soda, it is converted into *diethylhydroxyazoxazinedicarboxylic acid*, which crystallises in nodular aggregates of colourless tables, and melts at 186·5°. When this acid is distilled, best under diminished pressure, it loses carbonic anhydride, and yields a mixture of *ethylethoxyazoxazinecarboxylic acid* and *ethylethoxyazoxazine*, $\text{CH} \begin{array}{c} \text{C(OEt)} \\ \text{N} \cdot \text{O} \cdot \text{NEt} \end{array} \text{CH}$; these may be separated by distillation with steam, the latter being readily volatile. The former was obtained in colourless needles; it melts at 109°, and distils to a large extent unchanged; not so its silver salt, which yields the azoxazine. The latter is a colourless oil, boiling at 130·5° and 215° respectively under 32 mm. and 720 mm. pressure. With strong nitric acid, it yields a *nitro-derivative* as colourless plates melting at 69°; the same substance is obtained by the action of nitric acid on the monocarboxylic acid. C. F. B.

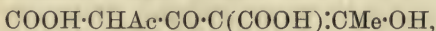
Action of Acetic Anhydride on Acetonedicarboxylic acid.
By H. V. PECHMANN and F. NEGER (*Annalen*, 273, 186—214).—

Carboxydehydracetic acid, $\text{CHAc} \cdot \text{CO} \begin{array}{c} \text{CO} \\ \text{CO} \cdot \text{O} \cdot \text{CMe} \end{array} \text{C} \cdot \text{COOH}$, is formed when acetonedicarboxylic acid is dissolved in acetic anhydride in the cold, and the solution then warmed for 5—10 minutes; it crystallises in lustrous plates, melts at 154°, and its alcoholic solution gives a brown coloration with ferric chloride. When heated alone, or boiled with alkalis, it is converted into dehydracetic acid (compare Abstr., 1892, 296), but when heated with water it yields dimethylpyrone; it is moderately stable towards oxidising agents, and decolorises alkaline

potassium permanganate only on long keeping. That its constitution is expressed by the above formula, is shown by a comparison of its method of formation with that of the analogous compound described below, as well as by the whole chemical behaviour of the substance; it must be assumed, therefore, that the action of acetic anhydride or of acetic chloride on acetonedicarboxylic acid results first in the formation of a compound of the composition



by the substitution of two hydrogen atoms in the methylene groups for two acetyl radicles; this compound may then be supposed to undergo intramolecular change into the tautomeric form,



from which carboxydehydracetic acid is produced by the elimination of 1 mol. H_2O . The properties of carboxydehydracetic acid accord well with this view of its constitution; it is a powerful acid, and has an electrical conductivity about 6000 times as great as that of dehydracetic acid, namely, $\kappa = 3.28$ (approximately). Although, on titration, it behaves as a monocarboxylic acid, molecular weight determinations by the cryoscopic method having given results in accordance with those required for the molecular formula $\text{C}_9\text{H}_6\text{O}_6$, it forms two classes of salts, containing one and two equivalents of metal respectively; the latter, however, behave like basic salts.

The *potassium* salt, $\text{C}_9\text{H}_7\text{O}_6\text{K}$, is deposited in slender, colourless needles when the acid is dissolved in excess of warm potash, and the solution strongly acidified with acetic acid; it has a neutral reaction, and seems to contain $2\text{H}_2\text{O}$, which are expelled at 105° . The basic salt, $\text{C}_9\text{H}_6\text{O}_6\text{K}_2$, prepared by dissolving the acid in excess of alcoholic potash, and then precipitating with alcohol, crystallises in colourless needles, and has an alkaline reaction. The two *sodium* salts are similar in properties to the potassium compounds. In moderately dilute solutions, both of the normal and basic salts, solutions of many metallic salts produce crystalline or amorphous precipitates. The *methylic* salt, $\text{C}_{10}\text{H}_{10}\text{O}_6$, can be prepared by treating the silver salt with methylic iodide, but it cannot be obtained from the potassium salt under these conditions, nor by treating the acid with methyl alcohol and hydrogen chloride; it crystallises in colourless plates, melts at 65° , and is slowly decomposed by cold water.

The formation of dehydracetic acid from the carboxy-derivative just described leads to the conclusion that dehydracetic acid has the constitution assigned to it by Feist. It follows also that the carboxy-derivative will give the same decomposition products as dehydracetic acid; when heated with concentrated sulphuric acid for example, it yields the lactone of triacetic acid described by Collie, and on treatment with concentrated hydrochloric acid, it is converted into the substance melting at 85° which is obtained from dehydracetic acid under like conditions.

Carboxydehydropropionylacetic acid, $\begin{array}{c} \text{CH}(\text{COEt})\cdot\text{CO} \\ \text{CO}-\text{O}-\text{CEt} \end{array} \gg \text{C}\cdot\text{COOH}$, can be obtained by treating acetonedicarboxylic acid with propionic

2 f 2

anhydride; it crystallises in colourless plates, melts at 114—115°, and resembles its homologue, carboxydehydracetic acid, very closely.

Dehydropropionylacetic acid, $\begin{array}{c} \text{CH}(\text{COEt}) \cdot \text{CO} \\ | \\ \text{CO} \cdot \text{O} \cdot \text{CEt} \cdot \text{CH} \end{array}$, is formed when a solution of the potassium salt of the preceding compound is evaporated; it crystallises in colourless needles, melts at 72°, and is similar to dehydracetic acid in properties.

Pentabromacetylacetone, $\text{C}_5\text{H}_3\text{Br}_5$, is produced, together with bromodehydracetic acid, when dehydracetic acid or its carboxy-derivative is treated with excess of dry bromine. It crystallises in slender, colourless needles, melts at 79°, and decomposes when heated, when kept, and when boiled with water; it is insoluble in alkalis, and gives no coloration with ferric chloride. Molecular weight determinations in benzene solution by the cryoscopic method gave values in accordance with those required by the above molecular formula; the constitution of the compound is probably expressed by the formula $\text{CH}_2\text{Br} \cdot \text{CO} \cdot \text{CBr}_2 \cdot \text{CO} \cdot \text{CHBr}_2$.

The *anilide*, $\begin{array}{c} \text{CHAc} \cdot \text{CO} \\ | \\ \text{CO} \cdot \text{O} \cdot \text{CMe} \end{array} > \text{C} \cdot \text{CO} \cdot \text{NHPh}$, crystallises in long, colourless needles, melts at 185°, is soluble in warm sodium carbonate, and its alcoholic solution gives a dark-red coloration with ferric chloride. It is decomposed into aniline and carboxydehydracetic acid by boiling soda.

Phenylmethylacetylpyridonone, $\text{CMe} < \begin{array}{c} \text{CH} - \text{CO} \\ | \\ \text{NPh} \cdot \text{CO} \end{array} > \text{CHAc}$, is produced, with evolution of carbonic anhydride, when the preceding compound is distilled under reduced pressure; it crystallises in lustrous plates, melts at 217—218°, and its alcoholic solution gives a red coloration with ferric chloride; it is soluble in soda, and even after the solution has been boiled for a long time, it is precipitated unchanged on adding acetic acid. The formation of this compound from the anilide may be explained by assuming that addition of the elements of water takes place, giving the intermediate product, $\text{COOH} \cdot \text{CHAc} \cdot \text{CO} \cdot \text{C}(\text{CO} \cdot \text{NHPh}) \cdot \text{CMe} \cdot \text{OH}$, which, after undergoing tautomeric change, is converted into phenylmethylacetylpyridonone and water.

The *anil*, $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_4$, can be obtained by boiling carboxydehydracetic acid with excess of aniline; it crystallises in slender, yellow needles, melts at 156—157°, and dissolves unchanged in cold soda, but is decomposed into aniline and carboxydehydracetic acid on boiling the solution.

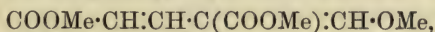
The *hydrazide*, $\begin{array}{c} \text{CHAc} \cdot \text{CO} \\ | \\ \text{CO} \cdot \text{O} \cdot \text{CMe} \end{array} > \text{C} \cdot \text{CO} \cdot \text{N}_2\text{H}_2\text{Ph}$, prepared by warming carboxydehydracetic acid with phenylhydrazine in glacial acetic acid solution, is a lemon-yellow, crystalline powder, melts at 190—191°, and is soluble in soda, being reprecipitated by carbonic anhydride; it is decomposed by boiling alkalis, and in its solution in concentrated sulphuric acid, ferric chloride and potassium dichromate produce a blue coloration. When carboxydehydracetic acid is boiled for a few minutes with excess of phenylhydrazine, it is converted into a sub-

stance which crystallises in lustrous, colourless needles, and melts at 259—260°; this compound gives no reaction with ferric chloride, is soluble in alkalis, and dissolves in warm, concentrated sulphuric acid with a dark-red coloration.

The experiments described above afford additional evidence that acetonedicarboxylic acid has not the properties of a hydroxy-compound, and no facts pointing to an opposite conclusion have yet been recorded, except those recently brought forward by Perkin (*Trans.*, 1892, 800). The evidence afforded by Perkin's measurements of the magnetic rotation of ethylic acetonedicarboxylate, however, is totally at variance with that obtained by a study of its chemical properties. If, as Perkin concludes, ethylic acetonedicarboxylate, may, under certain conditions, contain a hydroxy-group, the presence of the latter must be capable of proof by suitable chemical methods; hitherto, in spite of numerous attempts, it has been impossible to obtain any indication of its existence, so that ethylic acetonedicarboxylate may be regarded as a ketone for the same reasons as those which apply to the case of ethylic acetoacetate.

F. S. K.

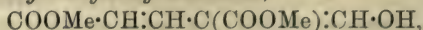
Coumalinic acid. By H. v. PECHMANN (*Annalen*, 273, 164—185).—*Methylic methoxymethyleneglutaconate*,



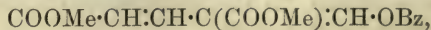
is formed when coumalinic acid (compare *Abstr.*, 1891, 1457) or its methylic salt is treated with hydrogen chloride under certain conditions which must be strictly observed in order to obtain good results. It crystallises in lustrous plates, melts at 62°, and is insoluble in water, but readily soluble in concentrated mineral acids; it gradually changes into a sticky, pasty mass when kept for a few days, a property common to other hydroxymethylene derivatives. Its alcoholic solution gives no reaction with ferric chloride or copper acetate, but yields a sparingly soluble amido-derivative on treatment with ammonia; when shaken with cold soda, the ethereal salt is converted into the sodium derivative of methylic hydroxymethyleneglutaconate. It is readily reconverted into coumalinic acid by boiling, concentrated hydrobromic acid, and, when treated with bromine, it yields methylic bromocoumalinate.

The formation of methylic methoxymethyleneglutaconate under the conditions mentioned above was hardly to be expected, and, judging from the behaviour of analogous compounds, the production of methylic hydroxymethyleneglutaconate appeared to be more probable; it must therefore be concluded that the methylation of the hydroxy-radicle is determined by the acid character of the hydroxymethylene group, which would appear to behave like the carboxyl-group. This assumption gains in probability by the fact that Claisen's hydroxymethylenecamphor is readily converted into ethoxymethylenecamphor on treatment with alcohol and hydrogen chloride; the ethoxy-compound obtained in this way boils at 265—268°, and is identical with the compound prepared by Claisen by treating hydroxymethylenecamphor with potash and ethylic iodide.

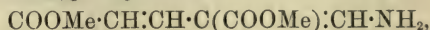
Ethylic ethoxymethyleneglutaconate is not easily obtained in crystals.

Methylic hydroxymethyleneglutaconate,

can be obtained by gently warming the methoxy-compound with dilute soda and decomposing the crystalline sodium derivative with dilute sulphuric acid. It crystallises in lustrous needles, melts at 88—89°, and is readily decomposed by warm water, being converted into methylic trimesate; unlike the methoxy-compound, it does not change even when kept for a long time. Its solution in dilute alcohol gives a bluish-violet coloration with ferric chloride, but not after it has been boiled; it dissolves in alkalis and alkali carbonates, giving colourless solutions which rapidly become yellow and acquire a greenish fluorescence, methylic trimesate being deposited in slender needles. It does not give the ordinary reactions of aldehydes. When boiled with concentrated hydrobromic acid, it yields coumalinic acid, and when heated alone, it is converted into methylic coumalinate and small quantities of other products. The benzoyl derivative,



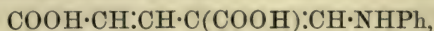
prepared by shaking the hydroxy-compound with soda and benzoic chloride, crystallises in colourless needles, melts at 90°, is insoluble in soda, and gives no reaction with ferric chloride.

Methylic amidomethyleneglutaconate,

is formed when the methoxy-compound is treated with concentrated alcoholic ammonia; it crystallises in flat, lustrous needles, sinters at 135°, melts at 140—141°, and is soluble in concentrated acids; when treated with acetic anhydride, it yields methylic trimesate.

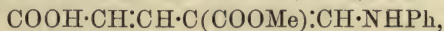
Methylic methamidomethyleneglutaconate, $\text{C}_9\text{H}_{13}\text{NO}_4$, prepared by treating the methoxy-compound with a concentrated solution of methylamine, crystallises in colourless needles, sinters at 140°, and melts at 143—144°.

Methylic anilidomethyleneglutaconate, $\text{C}_{14}\text{H}_{15}\text{NO}_4$, can be obtained by treating the hydroxy-, methoxy-, or benzoyl-derivative described above with aniline in methyl alcoholic solution, and also by heating the amido-compound with aniline hydrochloride. It is dimorphous; on quickly cooling its solution in hot alcohol, it is deposited in almost colourless needles, which sinter and turn yellow at 107—108°, melting completely at 117—118°; when the needles are left in the mother liquor, they change into small, yellow prisms which melt at 119—120°; the colourless is more readily soluble than the yellow modification, but both are insoluble in alkalis and dilute acids. It is not acted on by acetic anhydride, but, when boiled with soda, it yields small quantities of phenylpyridonecarboxylic acid. The corresponding *paratoluido*-derivative crystallises from alcohol in yellow prisms, and melts at 130°.

Anilidomethyleneglutaconic acid,

is obtained as a canary-yellow precipitate when coumalinic acid is treated with aniline in alcoholic solution at ordinary temperatures; it melts at 120—121°, and is either insoluble in or decomposed by the

ordinary solvents. It is decomposed by hot dilute acids and by boiling alkalis; when treated with dehydrating agents, it yields a well-characterised substance of the composition $C_{12}H_9NO_3$, which is dimorphous, and crystallises in lustrous, yellow plates or in rhombohedra, melting at $220-223^\circ$. The methylic hydrogen salt,



prepared from methylic coumalinate, melts at 140° , and has been previously described as an anil (Abstr., 1884, 1124; 1891, 1457); on prolonged boiling with alcohol, it is converted into a substance which crystallises in lustrous plates melting at 239° , and, when treated with dehydrating agents, it yields a compound of the composition $C_{13}H_{13}NO_4$; the latter crystallises in pale yellow prisms, and melts at $154-155^\circ$.

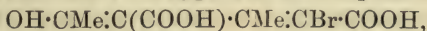
Methylic hydrogen paratoluidomethyleneglutaconate crystallises in sparingly soluble, yellow needles, and melts at $174-178^\circ$.

F. S. K.

Formation of Coumalin Rings. By F. FEIST (*Ber.*, 26, 747—764; compare Abstr., 1892, 584).—*Bromodimethylcoumalinic acid*, $C_8H_7BrO_4$, is prepared by heating dimethylcoumalinic acid (isodehydracetic acid) with bromine water; it crystallises from a mixture of benzene and alcohol in lustrous plates which melt at $161-162^\circ$, and may be sublimed without decomposition. On hydrolysis with potash,

a crystalline, bibasic acid, $\begin{array}{c} CMe-O-C-COOH \\ | \quad \quad | \\ C(COOH)-CMe \end{array}$, is formed, which decomposes at about 260° ; at lower temperatures, it is converted into dimethylfurfurancarboxylic acid (see below).

By the action of bromine water on dimethylcoumalinic acid at ordinary temperatures, carbonic anhydride is evolved, and an acid is obtained which melts at 122° , and closely resembles benzoic acid in appearance and properties; its vapour gives a green colour with a pine shaving moistened with hydrochloric acid. The production of this acid is preceded by the hydrolysis of bromodimethylcoumalinic acid and the formation of the hypothetical compound



which then decomposes spontaneously into $\alpha\beta$ -dimethylfurfuran-

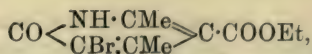
β -carboxylic acid, $\begin{array}{c} O-CMe \\ | \quad \quad | \\ CH:CMe \end{array} > C \cdot COOH$. This view of its constitution

is confirmed by its failure to react with either aqueous or alcoholic ammonia; the electrolytic conductivity, $\kappa = 0.00112$, $\mu\infty = 356$, is much lower than that of furfuran- α -carboxylic acid ($\kappa = 0.0707$), but similar differences are observed between corresponding compounds of the indole and pyrroline series.

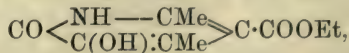
By the action of nitric acid on the preceding carboxylic acid, a non-nitrogenous compound is formed which crystallises in needles, and melts at 178° .

The author failed to observe the production of "bromomesiten-lactone" from dimethylcoumalinic acid and bromine water, as described by Hantzsch.

By the action of aqueous ammonia on ethylic dimethylbromocoumalinate, *ethylic bromodimethyl- α -pyridonecarboxylate*,

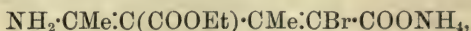


and *ethylic hydroxydimethyl- α -pyridonecarboxylate*,



are produced, together with a third compound which is precipitated from the mother liquors on acidification, melts at 195° , and has not been further investigated. The first salt is sparingly soluble in water, and crystallises in long, white needles melting at 155° ; the second crystallises in slender, lustrous plates, becomes red on exposure to air, melts at 118° , and readily sublimes.

By the action of ethylic dimethylbromocoumalinate on alcoholic ammonia, an unstable *ammonium salt*,



is formed; it is insoluble in ether, and, on treatment with hydrochloric acid, appears to be converted into ethylic bromodimethylpyridonecarboxylate (see above).

Symmetrical methyltrimethenyldicarboxylic acid, $\text{CHMe} < \begin{array}{c} \text{C} \cdot \text{COOH} \\ \parallel \\ \text{C} \cdot \text{COOH} \end{array} >$

is prepared by the hydrolysis of ethylic dimethylbromocoumalinate with potash; it crystallises from water, and, on sublimation, is deposited in needles which melt at 200° and decompose at slightly higher temperatures. A molecular weight determination by means of the boiling point method in ether agrees with the above formula. The acid is almost 10 times stronger than benzoic acid, as shown from its electrolytic conductivity, $\kappa = 0.05815$, $\mu_{\infty} = 356$. It decolorises bromine water and potassium permanganate solution, but does not react with hydrochloric acid or concentrated sulphuric acid; attempts to reduce it or to prepare an anhydride were unsuccessful. The *calcium salt* is deposited in monoclinic crystals containing $3\text{H}_2\text{O}$; the *barium salt* is crystalline; the *silver, lead, and mercurous salts* are amorphous. On heating the acid above its melting point, an amorphous, monobasic acid, $\text{C}_5\text{H}_6\text{O}_2$, is formed, of which the *copper* and *lead salts* are sparingly soluble.

Dibromomethyltrimethylenedicarboxylic acid, $\text{CHMe} < \begin{array}{c} \text{CBr} \cdot \text{COOH} \\ | \\ \text{CBr} \cdot \text{COOH} \end{array} >$, is

prepared from the trimethenyldicarboxylic acid by the action of bromine in excess at 100° , and is deposited from water in granular crystals melting at 240° with decomposition. *Asymmetrical methyl-*

trimethenyldicarboxylic acid, $\text{CMe} < \begin{array}{c} \text{C} \cdot \text{COOH} \\ | \\ \text{CH} \cdot \text{COOH} \end{array} >$, is obtained by the

reduction of the preceding compound by means of sodium amalgam; it crystallises from water, melts at 189° , and rapidly decolorises potassium permanganate solution and bromine water. The *calcium salt* is very readily soluble in water, and crystallises with $3\text{H}_2\text{O}$; the crystals are quite different in appearance from those of the calcium salt of the symmetrical acid.

By the action of bromine water on methyltrimethenyldicarboxylic acid at ordinary temperatures, *oxalbromobutyric acid*,



is formed, and melts at 138—139° with evolution of gas. The *lactonic acid*, $\text{CMe} \ll \begin{smallmatrix} \text{C}(\text{COOH}) \\ \text{CHBr} \cdot \text{CO} \end{smallmatrix} > \text{O}$, is prepared by treating symmetrical methyltrimethenyldicarboxylic acid with bromine water at higher temperatures, or by heating the preceding compound above its melting point; it is crystalline, melts at 168°, and is reconverted into the acid on boiling with alkali. On reduction of the bromolactone with sodium amalgam, *oxalbutyrolactonic acid*, $\text{CMe} \ll \begin{smallmatrix} \text{C}(\text{COOH}) \\ \text{CH}_2 - \text{CO} \end{smallmatrix} > \text{O}$, is formed, and melts at 141° without decomposition; by the action of hydroxylamine, symmetrical methyltrimethenyldicarboxylic acid appears to be regenerated.

J. B. T.

Thiocyanacetamide and Isothiohydantoin. By A. MIOLATI (*Gazzetta*, 23, i, 90—95).—*Thiocyanacetamide*, $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{SCN}$, is prepared by heating chloracetamide with potassium, ammonium, or barium thiocyanate in alcoholic solution; it separates on cooling the solution, and is ultimately obtained in almost colourless prisms melting at 112°. Ammonia is evolved on heating its solution in caustic soda, and on evaporating its solutions in acids, dioxithiazole is obtained; it yields hydrogen cyanide on reduction with zinc dust and acetic acid, and is soluble in chloroform, but practically insoluble in ether or benzene. The substance described by Claessen (*Abstr.*, 1878, 37) as thiocyanacetamide seems to be merely thiohydantoin.

Isothiohydantoin, $\begin{smallmatrix} \text{S} & \text{---} & \text{CO} \\ | & & | \\ \text{CH}_2 & \cdot & \text{C}(\text{NH}) \end{smallmatrix} > \text{NH}$, is obtained by dissolving thiocyanacetamide in slightly dilute sulphuric acid, and, after 24 hours, extracting the solution with ether; it forms long, white needles, melts at 71°, and is readily soluble in water or alcohol. Its aqueous solutions give precipitates with salts of silver and mercury. The prolonged action of acids converts it into dioxithiazole.

W. J. P.

Hydurilic and Deoxyamalic acids. By C. MATIGNON (*Compt. rend.*, 116, 642—645).—Baeyer regarded hydurilic acid as an ureide resulting from the condensation of barbituric and dialuric acids. Comparison of the heats of formation of the three acids shows that this change would result in the development of +10·3 Cal. when the acids are in the solid state. The author finds that when finely powdered and intimately mixed barbituric and dialuric acids are heated to the point at which carbonisation begins, hydurilic acid is readily formed. No such change seems to take place with solutions of the two acids.

Since the carbamide residues that exist in malonylcarbamide and tartronylcarbamide also persist in hydurilic acid, it would seem that the latter must have the constitution $\text{C}_2\text{H}_2 \left(\begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} > \text{O} \right)_2$.

Deoxyamalic acid.—If finely powdered amalic acid (tetramethylalloxantin) is heated in sealed tubes at $210\text{--}220^\circ$, deoxyamalic acid is obtained in much larger quantity than when the amalic acid is distilled as in Fischer's method. The acid is almost insoluble in both hot and cold water, but crystallises from hot water in small, brilliant, very hard crystals which seem to be square prisms terminated by pyramids.

The difference between the heats of combustion of amalic and deoxyamalic acid is $40\cdot65 \times 2$ Cal., a difference which seems to be characteristic of a compound and its hydroxyl-derivative. It would follow that tetramethylalloxantin is the dihydroxy-derivative of deoxyamalic acid. Alloxantin, however, is the dihydroxy-derivative of hydurilic acid, and hence it follows that deoxyamalic acid is the tetramethyl derivative of hydurilic acid, and its constitution is $\text{C}_2\text{H}_2\left(\begin{smallmatrix} <\text{CO}\cdot\text{NMe} \\ <\text{CO}\cdot\text{NMe} \end{smallmatrix} >\text{CO}\right)_2$.

The difference between the heats of combustion of hydurilic and deoxyamalic acids is $165\cdot8 \times 4$ Cal., and it has previously been shown that $165\cdot8$ Cal. is the characteristic difference for methyl derivatives when the methyl is united with nitrogen.

This view is supported by the following facts: Deoxyamalic acid decomposes boiling silver nitrate solution and yields an oxidation product which gives a blood-red coloration with ferric chloride. Solutions of the acid or its salts give with ferric chloride a beautiful green coloration, the formation of which is prevented by acids and alkalis. In presence of excess of ferric chloride, the green colour becomes red on boiling. These reactions are strictly analogous to those given by hydurilic acid. Hydurilic acid when oxidised yields alloxan, whilst deoxyamalic acid yields dimethylalloxan. The author has shown that hydurilic acid has three distinct acid functions. The tetramethyl derivative ought only to have two such functions, and as a matter of fact deoxyamalic acid yields a dipotassium salt, which forms hard, transparent, slightly yellowish crystals, but no tripotassium compound is produced.

C. H. B.

Thiophen of Crystallisation. By C. LIEBERMANN (*Ber.*, 26, 853—854).—Triphenylmethane, dibromo- β -dinaphthyl oxide, and α -truxillic acid chloride crystallise with thiophen, forming transparent, colourless crystals, which rapidly lose thiophen in the air and become opaque. The compounds with the first two substances have the composition $\text{CHPh}_3 + \text{C}_4\text{H}_4\text{S}$ and $\text{C}_{20}\text{H}_{12}\text{Br}_2\text{O} + \text{C}_4\text{H}_4\text{S}$ respectively.

C. F. B.

Electrolytic Reduction of Nitrobenzene dissolved in Sulphuric acid. By A. A. NOYES and A. A. CLEMENT (*Ber.*, 26, 990—992).—A current of 3 ampères (potential 5 volts) was passed for 15 hours at $80\text{--}90^\circ$ through a solution of 1 part of nitrobenzene in 4 parts of concentrated sulphuric acid. Paramidophenolortho-sulphonic acid was formed, the yield being 40 per cent. of the theoretical. If only 0.1 part of water is added, no sulphonic acid is

produced, but the sulphate of paramidophenol, as Gattermann and Koppert found.

Neither orthonitrotoluene nor α -nitronaphthalene yields an insoluble sulphonic acid; both yield a sulphate of a readily oxidisable base.

C. F. B.

Diiodometaxylylene obtained from Iodometaxylylene and Sulphuric acid. By A. TÖHL and E. BAUCH (*Ber.*, 26, 1105—1108; compare Abstr., 1890, 1106).—The formation of durenene by the action of methylic iodide on the diiodo-xylene (*loc. cit.*) shows that the latter has the constitution $[Me_2:I_2 = 1:3:4:6]$. The iodometaxylylene-sulphonic acid (Abstr., 1891, 73) forms a sodium salt which crystallises in silky needles containing $2H_2O$, a sulphochloride melting at 74° , a sulphonamide melting at 176° , and sulphanilide melting at 153° .

The diiodo-xylene dissolves slowly in fuming sulphuric acid forming tetraiodo-xylene melting at 128° , and a diiodo-xylenesulphonic acid. The latter gives a sodium salt which crystallises with $2H_2O$, a barium salt which is sparingly soluble in water, a sulphochloride melting at 85 – 87° , and a sulphonamide melting at 242 – 245° with decomposition. The sodium salt, on reduction with zinc dust and ammonia, gives 1:3:4-metaxylenesulphonic acid; this shows that a shifting of one of the iodine atoms of the diiodo-xylene must have taken place during the sulphonation.

A. R. L.

Reactions of Iodomesitylene. By A. TÖHL and R. ECKEL (*Ber.*, 26, 1099—1104).—By shaking iodomesitylene (Abstr., 1892, 96) with concentrated sulphuric acid, diiodomesitylene, which crystallises in yellowish-white needles and melts at 82 – 83° , is obtained, together with mesitylenesulphonic acid, the sulphonamide of which melts at 142° . Fuming sulphuric acid converts both iodomesitylene and diiodomesitylene into triiodomesitylene, which crystallises in stout, yellowish-white prisms, and melts at 208° , and mesitylenesulphonic acid. When sulphuric anhydride is allowed to condense into a flask containing iodomesitylene, the products are diiodomesitylene and iodomesitylenesulphonic acid; whilst from diiodomesitylene and sulphuric acid there are formed triiodomesitylene and the last-mentioned sulphonic acid. The barium salt crystallises with 1 mol. H_2O , and begins to decompose at 130° , the lead salt is very sparingly soluble in water, and the sulphonamide melts at 156° .

Nitroiodomesitylene is obtained by the action of a mixture of fuming and ordinary nitric acid on iodomesitylene; it crystallises in white needles, and melts at 73 – 74° . Dinitroiodomesitylene, melting at 205 – 206° , is formed by the action of fuming nitric acid on iodomesitylene. Nitrodiiodomesitylene, melting at 183° , is obtained by the action of a mixture of ordinary and fuming nitric acid on diiodomesitylene. When triiodomesitylene is warmed with a mixture of nitric and sulphuric acids, dinitriiodomesitylene and trinitromesitylene (m. p. 230°) are formed. Chlorosulphonic acid converts iodomesitylene and diiodomesitylene into trichloromesitylene; the latter is also formed, together with the intermediate chlorodiiodomesitylene (m. p.

167°) and *dichloriodomesitylene* (m. p. 183°), when mono- and di-iodomesitylene are treated with chlorine. A. R. L.

Paradiethylbenzene. By H. FOURNIER (*Bull. Soc. Chim.* [3], 7, 651—653).—The product of the action of ethylic bromide on benzene in the presence of aluminium chloride contains, contrary to Voswinkel's statement, more metadiethylbenzene than of the para-derivative. The mixture is sulphonated and then converted into barium salt (Voswinkel, *Abstr.*, 1889, 38); on crystallising this from water, the meta-derivative separates out, whilst the impure para-derivative which remains in solution is purified by conversion into the cadmium salt (*Abstr.*, 1889, 493). To regenerate the hydrocarbon, the sodium salt is heated with phosphoric acid of 60° B. Paradiethylbenzene melts at -35°. The *tribromo*-derivative melts at 105—106°, and the *tetrabromo*-derivative melts at 157°. A. R. L.

Behaviour of Halogen Derivatives of ψ -Cumene towards Sulphuric acid. By A. TÖHL and A. MÜLLER (*Ber.*, 26, 1108—1113).—Symmetrical fluoro- ψ -cumene (*Abstr.*, 1888, 362) is only sulphonated by warming it with concentrated sulphuric acid, and, unlike the chloro-, bromo-, and iodo-derivatives, one *sulphonic acid* only is formed; this melts at 115—116°, forms a *barium* salt sparingly soluble in water, which crystallises with 1H₂O, a *sodium* salt crystallising with 4H₂O, a *sulphochloride* melting at 36—37°, and a *sulphonamide* melting at 174°.

When fluoro- ψ -cumene is treated with chlorine in the presence of iodine, fluorodichloro- ψ -cumene, which crystallises in long, silky needles, and melts at 150°, represents the solid portion of the product; whilst the liquid portion is converted by chlorosulphonic acid into a *fluorochloro- ψ -cumenesulphonic acid*, which forms a *sodium* salt sparingly soluble in water, an oily *sulphochloride*, and a *sulphonamide* melting at 171°. The fluorochloro- ψ -cumene, regenerated from the sodium salt by heating it with concentrated hydrochloric acid at 180°, is a liquid boiling at 205° and solidifying when cooled; on treatment with fuming sulphuric acid, it yields fluorodichloro- ψ -cumene and fluoro- ψ -cumenesulphonic acid (see above). By the action of bromine on fluoro- ψ -cumene there are formed *fluorodibromo- ψ -cumene* melting at 143—144°, and a liquid which, when treated with chlorosulphonic acid, yields *fluorobromo- ψ -cumenesulphonic acid*; the *sodium* salt crystallises with 2H₂O, and the *sulphonamide* melts at 149°. The regenerated fluorobromo- ψ -cumene yields with sulphuric acid fluorodibromo- ψ -cumene and fluoro- ψ -cumenesulphonic acid.

A mixture of ordinary and fuming nitric acid converts fluoro- ψ -cumene into *nitrofluoro- ψ -cumene*, a liquid which solidifies at 5°; whilst fuming nitric acid converts it into an acid and *dinitrofluoro- ψ -cumene* which crystallises in colourless needles and melts at 74—76°. *Fluoro- ψ -cumidine* is prepared by reducing nitrofluoro- ψ -cumene with iron and acetic acid; its *acetyl* derivative melts at 118°. By the diazo-reaction, it may be converted into *fluoriodo- ψ -cumene*, an oil which did not solidify when cooled to 0°, and decomposes with liberation of iodine on treatment with sulphuric acid. A. R. L.

Pentethylbenzene. By H. FOURNIER (*Bull. Soc. Chim.* [3], 7, 653—654).—When pentethylbenzene (Jacobsen, *Abstr.*, 1889, 40) is heated in an oil-bath at 120° with benzylic chloride and a little aluminium chloride, the product treated with water, extracted with ether, and the ethereal solution distilled, *benzylpentethylbenzene*, $C_6H_5 \cdot CH_2Ph$, may be isolated from the portion passing over above 300° . It crystallises in white needles, melts at $88-89^{\circ}$, and boils above 360° .
A. R. L.

Compounds of Alkali Phenoxides with Phenol. By DE FORCRAND (*Compt. rend.*, 116, 586—588).—Calorimetric determinations indicate that potassium phenoxide combines with phenol to form the compound $C_6H_5 \cdot OK, 3C_6H_5 \cdot OH$, but forms no definite compound containing a higher or a lower proportion of phenol.

Sodium phenoxide forms two compounds, $C_6H_5 \cdot ONa, 3C_6H_5 \cdot OH$ and $C_6H_5 \cdot ONa, 6C_6H_5 \cdot OH$.

It is noteworthy that, in additive compounds such as alcoholates, phenolates, or hydrates, the ratio 1:3 is very common; that frequently a potassium derivative forms only one such additive compound, whilst the corresponding sodium derivative forms two or more; and that, although the sodium derivative may combine with a larger number of molecules of the phenol, alcohol, &c., the additive compound formed by the potassium derivative is usually more stable.

C. H. B.

Symmetrical Dimethoxyquinone. By G. CIAMICIAN and P. SILBER (*Ber.*, 26, 784—786).—Symmetrical trimethoxybenzene is readily prepared by fusing either methylhydrocotoïn or methylpyrocotoïn with potash (compare this vol., i, 417); on oxidation with chromic anhydride in glacial acetic acid solution, it is converted into symmetrical dimethoxyquinone (m. p. 249°), which is identical with Hesse's "quinone."
J. B. T.

Metamidodialkylorthotoluidines. By A. BERNTHSEN (*Ber.*, 26, 992—993).—A reply to Weinberg, this vol., i, 265.

Compounds containing Double Linking between Nitrogen and Carbon. By A. HANTZSCH (*Ber.*, 26, 926—929).—No case of stereoisomerism has been observed in the examination of the following compounds.

The compound $OMe \cdot C_6H_4 \cdot CPh \cdot N \cdot C_6H_4 \cdot NMe_2$ is obtained by mixing anisyl phenylketochloride (1 mol.) with amidodimethylaniline (3 mols.) in chloroform solution. It crystallises in sulphur-yellow crystals, melts at 116° , is resolved into the ketone and base by mineral acids, and yields a hydrochloride which is decomposed by water.

Phenylbenzimidophenyl ether, $OPh \cdot CPh \cdot N \cdot Ph$, is obtained by mixing benzanilidoimide chloride and sodium phenoxide suspended in absolute ether. It forms colourless crystals, melts at 104° , and is decomposed by warm, concentrated hydrochloric acid into aniline and phenylic benzoate.

Tolylbenzimidophenyl ether, $OPh \cdot CPh \cdot N \cdot C_6H_4Me$, melts at 120° , and yields a crystalline hydrochloride, which is decomposed by water.

The compound $\text{OPh}\cdot\text{CPh}\cdot\text{N}\cdot\text{COOEt}$ is obtained by converting ethylic benzoylcarbamate into the chloride, $\text{CPhCl}\cdot\text{N}\cdot\text{COOEt}$, with phosphoric chloride, and then treating it with sodium phenoxide. It melts at 91° .

Benzoylurethane cannot be prepared from sodium urethane and benzoic chloride. When these compounds are mixed, they yield ethylic dibenzoylcarbamate, $\text{NBz}_2\cdot\text{COOEt}$, which crystallises in large, rhombic tablets, and melts at 103° , and a compound of the composition $\text{C}_{17}\text{H}_{13}\text{NO}_3$, which is more soluble in alcohol than ethylic dibenzoylcarbamate, crystallises in white needles, and melts at 190° .

E. C. R.

Azo-derivatives of Catechol. By O. N. WITT and F. MAYER (*Ber.*, **26**, 1072—1076).—The author has shown (D.R.-P. 49,872 and 49,979) that β -naphthaquinol combines with diazo-compounds to form azo-dyes, a fact which stands in antithesis to Griess' rule that such compounds can only be obtained from metadihydroxy-, and metadiamido-derivatives.

Benzeneazocatechol, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{N}_2\text{Ph}$, is obtained by mixing an alcoholic solution of catechol with a concentrated solution of diazobenzene chloride, and after a while pouring the mixture on to ice; the precipitate is crystallised first from a solution of sodium acetate, and subsequently from alcohol. When its solutions are allowed to slowly cool, it separates in garnet-red needles having a blue surface-lustre, whilst by rapidly cooling its solutions, it separates in golden leaflets which, if left in contact with the liquid, pass into the red modification. It melts at 165° with decomposition, is soluble in alkalis, and dyes cotton mordanted with alumina golden-yellow.

Paratolueneazocatechol, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$, forms copper-red, lustrous leaflets, melts at 175° with decomposition, and is more readily soluble in water than the benzene derivative.

Paranitrobenzeneazocatechol, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$, colours alumina mordants red and iron and chromium mordants deep brown; it is reduced to dihydroxyamidoazobenzene by ammonium sulphide. The diacetyl derivative melts at 126 — 127° .

The compound $\text{SO}_3\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$ is obtained by dropping freshly-prepared diazobenzeneparasulphonic acid into an aqueous solution of catechol, and precipitating with sodium acetate; its aqueous solution gives crystalline precipitates on the addition of calcium and barium salts, and intense colorations with salts of the iron group. Wool mordanted with alumina is dyed golden-yellow, and mordanted with chromium, reddish-brown.

Benzoylcatechol, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$, forms lustrous, white needles, melts at 130 — 131° , and forms an azo-compound which when warmed with alkali yields benzeneazocatechol.

A. R. L.

Action of Hydrazine Hydrate on Organic Halogen Compounds. By R. v. ROTHENBURG (*Ber.*, **26**, 865—868).—It has been previously shown by Schöfer (*Inaug. Diss.*, Kiel, 1892) that hydrazine hydrate does not act on ethylic chloracetoacetate in a similar manner to ammonia, but yields hydrazine monohydrochloride and nitrogen as the sole recognisable products. The author finds that with benzoic

chloride it behaves like ammonia, yielding the benzoylhydrazine already described, together with either the mono- or di-hydrochloride of hydrazine. With methylic iodide, it yields ethylene and hydrazine dihydriodide, with ethylic iodide, ethylene and trihydrazine dihydriodide, and with isoamylic iodide, the same salt and isoamylenes. Benzylic chloride yields, in addition to hydrazine monohydrochloride, a mixture of dibenzyl, stilbene, and tolane, the latter being probably derived from the benzal chloride usually present in commercial benzylic chloride.

Chloroform is not acted on by hydrazine hydrate, even at the boiling point, whilst iodoform appears to undergo a slight reduction.

H. G. C.

New Method of preparing Unsymmetrical Derivatives of Phenylhydrazine. By O. WIDMAN (*Ber.*, 26, 945—948).—When β -acetylphenylhydrazine, $\text{NHPh}\cdot\text{NHAc}$, is acetylated with acetic chloride, a second acetyl group enters in the α -position, and when the diacetyl derivative is boiled with dilute acid, hydrolysis occurs and the β -acetyl group is displaced. In this way, several α -acidyl derivatives of phenylhydrazine, including some compounds already known, have been prepared; the melting points of these are given, and further experimental details are promised.

A. R. L.

The Hydrochlorides of Stereoisomeric Aldoximes. By A. HANTZSCH (*Ber.*, 26, 929—932).—The hydrochlorides of both synaldoximes and antialdoximes are converted by water into antialdoximes, and by aqueous alkali carbonates or ammonia into synaldoximes. This seems to indicate that the two stereoisomerides yield identical hydrochlorides. From the following results, however, it is proved that this is not the case. When anisantaldoxime and cuminaldoxime are converted into hydrochlorides by treating their ethereal solutions with hydrogen chloride, and when the dry salts are treated with a solution of ammonia in absolute ether, anisantaldoxime (m. p. 61°) and cuminaldoxime (m. p. 58°) are regenerated. Similarly the synaldoximes after the same treatment are recovered as synaldoximes.

If anisantaldoxime hydrochloride, suspended in dry ether, is treated with dry ammonia, it yields pure anis-synaldoxime. Under the same conditions, cuminsynaldoxime yields cuminaldoxime, and paranitrobenzantaldoxime and paranitrobenzsynaldoxime yield a mixture of the two isomerides.

E. C. R.

Oxidation and Sulphonation of Organic Compounds by Ammonium Hydrogen Sulphate. By M. LACHAUD and C. LÉPIERRE (*Bull. Soc. Chim.* [3], 7, 649—651).—When naphthalene, pyridine, aniline, &c., are added to fused ammonium hydrogen sulphate, they are dissolved, and the product is soluble in water. In the case of aniline, on heating the melt to between 200° and 350° , a series of colouring matters, ranging from red, violet, and blue to black, are formed, some of which dye silk directly.

A. R. L.

Unsymmetrical Dibenzylthiocarbamide. By G. MAZZARA (*Gazzetta*, 23, i, 37—43).—On mixing benzene solutions of thio-

carbonyl chloride and dibenzylamine, heat is evolved, and a mixture of dibenzylamine hydrochloride and *dibenzylthiocarbamic chloride*, $\text{CSCl} \cdot \text{NBz}_2$, separates; the latter forms a yellow, hygroscopic, crystalline mass, which melts at $49\text{--}50^\circ$, and is very soluble in benzene, alcohol, or chloroform. When heated at 100° with alcoholic ammonia, it yields unsymmetrical dibenzylthiocarbamide. This compound forms colourless laminæ, melts at $134\text{--}135^\circ$, and when prepared by heating dibenzylamine thiocyanate is also obtained colourless, and of the melting point given above, not, as stated by Salkowski (Abstr., 1891, 1474) in yellow crystals melting at 141° .

Dibenzylamine thiocyanate is obtained by the action of aqueous thiocyanic acid on dibenzylamine, or by mixing solutions of dibenzylamine hydrochloride and potassium thiocyanate; it melts at $156\text{--}157^\circ$, not at $164\text{--}165^\circ$, as stated by Salkowski (*loc. cit.*), and is far more soluble in water than unsymmetrical dibenzylthiocarbamide. On heating either the thiocyanate or the thiocarbamide at 140° for some time, a mixture of the two isomerides is obtained; the conversion of the one substance into the other is therefore a reversible change at this temperature. The thiocyanate gives the well-known red coloration with ferric chloride, whilst the thiocarbamide does not.

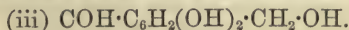
W. J. P.

Gallanilide and its Triacetyl and Tribenzoyl Derivatives.

By P. CAZENEUVE (*Compt. rend.*, 116, 698—700).—Aniline gallate, when heated at $105\text{--}110^\circ$, loses carbonic anhydride before losing water, thus forming gallanilide. If, however, gallo-tannic acid is heated with excess of aniline at about 150° for an hour, gallanilide is formed, and after treating the product with dilute hydrochloric acid, can be crystallised from dilute alcohol. After repeated crystallisation, it forms large lamellæ, which lose 2 mols. H_2O at 100° , and when anhydrous have the composition $\text{C}_6\text{H}_2(\text{OH})_3\text{CO} \cdot \text{NHPh}$. It melts at 205° without any marked discoloration, and without any evolution of gas. It is only slightly soluble in cold water, but dissolves readily in hot water, and the solution gives a blue coloration with ferric chloride. It dissolves easily in alcohol of 93° , and also somewhat readily in ether of 65° , but it is insoluble in chloroform, benzene, and light petroleum. It dissolves better in alkalis, forming coloured solutions, but the alteration is only partial. It is not affected when boiled with sodium hydroxide solution for 10 minutes, and it is only slowly attacked by dilute sulphuric and hydrochloric acids. When heated at 150° for an hour with twice its weight of concentrated hydrochloric acid, gallanilide yields gallic acid and aniline. With acetic anhydride, it yields a triacetyl derivative, which crystallises from alcohol in very light, small, white needles melting at $160\text{--}161^\circ$ to a colourless liquid, which decomposes with evolution of acetic acid. The acetyl derivative gives no coloration with ferric chloride. Benzoic chloride yields a tribenzoyl derivative, which crystallises from boiling toluene in small, white needles melting at 181° . This compound is insoluble in most solvents, and cannot be distilled without decomposition.

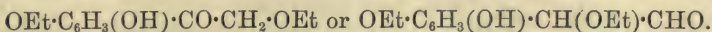
C. H. B.

Quercetin Derivatives. By J. HERZIG and T. V. SMOLUCHOWSKI (*Monatsh.*, 14, 39—52 and 53—55; compare *Abstr.*, 1888, 1309; 1890, 64; 1891, 1386.—*Constitution of Fisetol.*—The method of preparing fisetol from fisetin has been already described (*loc. cit.*). Fisetol, $C_8H_8O_4$, contains three hydroxyl groups, and the fourth oxygen atom is evidently present as a carbonyl or formyl group, since the compound reacts with phenylhydrazine. As it is evidently a resorcinol derivative, it must have the constitution: (i) $C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot OH$; (ii) $C_6H_3(OH)_2 \cdot CH(OH) \cdot COH$; or, less probably,



Methylfisetol, $C_8H_6O_2(OMe)_2$, when heated in a reflux apparatus with alcoholic phenylhydrazine for three hours, gives the compound $C_{16}H_{18}O_3N_2$, which crystallises from hot alcohol in shining yellow scales, and melts at 55—57°.

With hydroxylamine hydrochloride, ethylfisetol forms the equally well characterised compound $C_{12}H_{17}NO_4$, which crystallises from dilute alcohol in beautiful, white needles, and melts at 105—107°. On oxidation with potassium permanganate in alkaline solution, ethylfisetol yields a mixture of *ethylresorcylglyoxylic acid* and *ethylresorcyclic acid*. The former, $C_{10}H_{17}O_5$, crystallises from water and benzene in white scales, melts at 65—68°, contains only one of the ethoxyl groups present in ethylfisetol, and is converted on ethylation into the diethoxy-acid, $C_8H_4O_3(OEt)_2$, which crystallises from benzene in stout, white needles, and melts at 128—130°. It readily reacts with hydroxylamine, giving rise to a compound which melts at about 150°. The acid, $C_8H_6O_5$, from which it is derived must therefore have the formula $COH \cdot C_6H_2(OH)_2 \cdot COOH$, if the first or second of the constitutions suggested above for fisetol be correct. The probability of the third constitution for fisetol being correct is extremely small, since that would assume the oxidation of an alkyl group to carboxyl, whilst a formyl-group remained intact, a most improbable occurrence. Each of the oxidation products of ethylfisetol contains only one ethoxyl-group; the second ethoxyl-group present in ethylfisetol is, therefore, most probably contained in the side chain, which is removed by oxidation. It follows that ethylfisetol must contain free hydroxyl, and that it should be represented by one of the following formulæ:—



The latter, however, is most improbable, since no carboxylic acid corresponding to it is found amongst the products of oxidation.

Composition of Quercitrin.—The authors have made a number of analyses of quercitrin, and have obtained results which closely agree with the formula $C_{21}H_{22}O_{12}$, previously found by Liebermann and Hamburger (*Abstr.*, 1879, 944). Quercitrin is resolved by hydrolysis into equal molecular proportions of quercetin and rhamnose.

G. T. M.

Isomeric Amidobenzoic acids. By O. DE CONINCK (*Compt. rend.*, 116, 510—512 and 588—591).—The author has determined the quantity of each of the three isomeric amidobenzoic acids dissolved

in two hours, at a temperature of about 10° , by 10 c.c. of various solvents, namely, hydrochloric, hydrobromic, and hydriodic acids, dilute nitric, sulphuric, and acetic acids, glacial acetic acid, dilute ammonia solution, dilute lime water, dilute baryta solution, light petroleum, benzene, carbon bisulphide, ethylic acetate, and water. The experiments with water were made at $12-14^{\circ}$. Light petroleum boiling at $35-65^{\circ}$ dissolves no trace of any of the three isomerides.

The results show that the three isomerides differ distinctly in solubility, but differ in pairs, one of the three being either more or less soluble in a particular solvent than the other two. For example.

	Ortho-.	Meta-.	Para-.
Hydrochloric acid	0.929	1.283	0.980
Hydrobromic acid	0.1753	0.0504	0.0751
Hydriodic acid	0.589	0.574	1.193
Nitric acid, dilute	0.8775	0.1950	0.1484
Sulphuric acid, dilute....	0.380	0.336	0.382
Acetic acid, ,, 	0.0370	0.0764	0.0454
Water	0.0340	0.0568	0.0336

In the case of the alkali solvents, this differing in pairs is less distinctly marked.

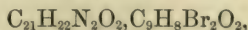
C. H. B.

Orthomethamidobenzoic acid. By G. FORTMANN (*J. pr. Chem.* [2], 47, 400).—Orthomethamidobenzoic acid melts at 179° , but begins to soften at 170° , which has heretofore been given as its melting point. By treating its hydrochloride with sodium nitrite in water, *nitrosorthomethamidobenzoic acid*, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NO}$, is obtained; it crystallises in small prisms, and melts at 128° .

Orthacetylmethamidobenzoic acid is a crystalline powder which melts at 192° .

A. G. B.

Optically Active Cinnamic acid Dibromides. By C. LIEBERMANN and A. HARTMANN (*Ber.*, 26, 829—833; compare this vol., i, 268).—Inactive cinnamic acid dibromide, $\text{C}_9\text{H}_8\text{Br}_2\text{O}_2$, has, as before described, been separated into dextro- and lævo-rotatory constituents by crystallising the strychnine salts of these acids,



from an alcoholic solution containing the base and acid in the proportions $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2 : 2\text{C}_9\text{H}_8\text{Br}_2\text{O}_2$, the crystallisation being started by the introduction of a few crystals of the particular constituent which it was desired to separate.

By repeated application of this process, the inactive dibromide was split up into two constituents, with rotations $[\alpha]_D = +67-67.5^{\circ}$ and -65.7° respectively. The + and - dibromides appear to form complementary hemihedral crystals, which have the same crystallographical constants as the inactive substance; the latter, however, exhibits some additional faces. No evidence has yet been obtained of the existence of a third and a fourth active dibromide, such as are predicted by Van't Hoff's theory.

C. F. B.

Optically Active Cinnamic acid Dichlorides. By C. LIEBERMANN and H. FINKENBEINER (*Ber.*, **26**, 833—834).—Inactive cinnamic acid dichloride has been separated, although not so readily, into its optically active constituents by the method adopted in the case of the corresponding dibromide (see preceding abstract). The process of fractionation is not yet complete; the maximum rotations so far obtained are $[\alpha]_D = +67.3^\circ$ and -44° . C. F. B.

Orthonitrobenzyl Derivatives. By C. BECK (*J. pr. Chem.* [2], **47**, 397—400).—Orthonitrobenzylphthalimide melts at 207° (Gabriel gives $217.5\text{--}219^\circ$; Abstr., 1887, 1037).

Orthonitrobenzylsuccinimide, $C_{11}H_{10}N_2O_4$, is made by heating an alcoholic solution of succinimide and sodium hydroxide with orthonitrobenzyl chloride for 12 hours in a reflux apparatus; it crystallises in nacreous laminæ, and melts at 130° .

The best method for preparing orthonitrobenzylamine sulphate is to heat the phthalimide with sulphuric acid, filter off the phthalic acid, make alkaline with caustic soda, extract with ether, and shake the ethereal solution with dilute sulphuric acid; it crystallises in long, white tables. The normal salt is sparingly soluble in alcohol, whilst the acid salt dissolves freely in alcohol and water. The alcohol is easily obtained from the amine by the action of nitrous acid.

A. G. B.

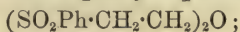
Conversion of Phthalide Derivatives into those of $\alpha\gamma$ -Diketohydrindone. By S. GABRIEL and A. NEUMANN (*Ber.*, **26**, 951—955).—A method of preparing phthalylacetic acid,



is described in which potassium acetate is used instead of sodium acetate, whereby the yield is augmented. When the acid is made into a paste with wood spirit, and poured into a solution of sodium in wood spirit, the *disodium salt* of $\alpha\gamma$ -diketohydrindenecarboxylic acid, $C_6H_4 < \begin{array}{c} CO \\ CO \end{array} > CNa \cdot COONa + H_2O$, separates as a yellow precipitate; the *sodium salt*, $C_{10}H_5O_4Na + 2H_2O$, is precipitated on the addition of acetic acid to an aqueous solution of the disodium salt. When the disodium salt is warmed with dilute hydrochloric acid, carbonic anhydride is evolved and $\alpha\gamma$ -diketohydrindene (Abstr., 1888, 1194) is obtained; whilst by heating it in a sealed tube at 100° with methyl alcohol and methylic iodide, dimethyl- $\alpha\gamma$ -diketohydrindene (Abstr., 1889, 1068) is formed. Benzalphthalide and ethylidenephthalide behave in a similar manner to phthalylacetic acid.

A. R. L.

Diphenylsulphonethylic and Ditolylsulphonethylic Oxides. By R. OTTO and J. TRÖGER (*Ber.*, **26**, 944—945).—The hydroxyethylphenylsulphone prepared by Otto (*J. pr. Chem.* [2], **30**, 171 and 321) is now found to contain *diphenylsulphonethylic oxide*,



it melts at 69—70°. The *homologous compound* (m. p. 83—84°) was also separated from hydroxyethyltolylsulphone (*loc. cit.*). The authors regard the ethers as formed at the same time as the alcohols, and discard the view that they have been derived from the latter by spontaneous dehydration.

A. R. L.

Anilides of Benzene- and Paratoluene-sulphonic acids; Phenyl- and Paratolyl-sulphonoxy-sulphobenzide. By R. OTTO (*J. pr. Chem.* [2], 47, 367—374).—Phenylsulphoneanilide, paratolylsulphoneanilide, and phenylsulphonemethylanilide (m. p. 79—80°) have been re-examined, and their crystallographical measurements, together with those of the undermentioned anilides, are recorded.

Paratolylsulphonemethylanilide, $\text{NMePh}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$, melts at 94—95°; it is insoluble in water, but dissolves easily in boiling alcohol, benzene, and ethylic acetate.

Phenylsulphonethylanilide, $\text{NEtPh}\cdot\text{SO}_2\text{Ph}$, is a yellowish, viscid oil, insoluble in water, but soluble in ether, alcohol, and benzene.

Paratolylsulphonethylanilide, $\text{NEtPh}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$, melts at 87—88°, is insoluble in water, but soluble in boiling alcohol, boiling benzene, and ethylic acetate.

The above anilides were prepared from the corresponding substituted anilines and sulphonic chlorides.

Phenylsulphonoxy-sulphobenzide, $\text{SO}_2(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Ph})_2$, is prepared from oxysulphobenzide and benzenesulphonic chloride; it forms aggregates of silky crystals, melts at 131—132°, and dissolves in hot alcohol and ethylic acetate, but not in water.

Paratolylsulphonoxy-sulphobenzide, from oxysulphobenzide and paratoluenesulphonic chloride, forms feebly lustrous, ill-defined needles, melts at 171—172°, and dissolves in boiling ethylic acetate and boiling glacial acetic acid.

A. G. B.

Non-existence of Stenhouse's Phenylthiosulphuric acid. Sulphonic acids of Phenyl Sulphide. Bunte's Salt. By R. OTTO and J. TRÖGER (*Ber.*, 26, 993—996).—The substance obtained by heating phenyl sulphide with an equal volume of strong sulphuric acid on the water bath is not phenylthiosulphuric acid, $\text{OH}\cdot\text{SO}_2\cdot\text{SPh}$, as Stenhouse stated, but *thiodibenzenedisulphonic acid*, $\text{C}_{12}\text{H}_8\text{S}(\text{SO}_3\text{H})_2$; its *barium salt*, with H_2O , and *chloride*, melting at 157°, were prepared. By acting on phenyl sulphide (1 mol.) with chlorosulphonic acid (2 mols.), an isomeric (or identical?) disulphonic acid was obtained, of which the *chloride* melts at 157°, but the *barium salt* crystallises with $3\text{H}_2\text{O}$. With 1 mol. of chlorosulphonic acid, a *thiophenylbenzenesulphonic acid*, $\text{SPh}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, was obtained; the *chloride* melts at 66—68°, the *amide* at 129—130°.

Bunte's salt (sodium ethylic thiosulphate) can be obtained in a yield of 90 per cent. by shaking ethylic bromide with a saturated solution of sodium thiosulphate at 35° until the former has all disappeared, evaporating the solution, and extracting the residue with alcohol.

C. F. B.

"Leucotin" and Cotogenin. By G. CIAMICIAN and P. SILBER (*Ber.*, 26, 777—784; compare Abstr., 1892, 62 and 873).—Jobst and Hesse obtained a compound, which they termed "leucotin," from paracoto bark; the authors have reinvestigated this substance, and find that it consists of a mixture of almost equal parts of methylprotocotoin, $\text{CH}_2\langle\text{O}\rangle\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_2(\text{OMe})_3$, and methylhydrocotoin, $\text{C}_6\text{H}_2\text{Bz}(\text{OMe})_3$, together with about 10 per cent. of paracotoin. The last of these is removed by treatment of "leucotin" with potash, and the other two compounds are separated by repeated extraction of the residue with ether at the ordinary temperature; methylprotocotoin being the more readily soluble.

Cotogenin, $\text{C}_{14}\text{H}_{14}\text{O}_5$ (m. p. 210°), was prepared by Jobst and Hesse by fusing "leucotin" or "oxyleucotin" (methylprotocotoin) with potash, orthodihydroxybenzaldehyde [1 : 3 : 4] being also formed; the cotogenin obtained by the fusion of pure methylprotocotoin with potash melts at 217° , but is otherwise identical in properties with Jobst and Hesse's compound, and proves to be *dihydroxybenzoyltrimethoxybenzene*, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CO}\cdot\text{C}_6\text{H}_2(\text{OMe})_3$. The *diacetate* crystallises in stellate prisms melting at 120° . The presence of orthodihydroxybenzaldehyde in the products of fusion could not be detected.

J. B. T.

Carbazacridines. IV. Oxidation of Phenylcarbazacridine. By D. BIZZARI (*Gazzetta*, 23, i, 1—9; compare Abstr., 1891, 219; 1892, 617).—Phenylcarbazacridine is slowly oxidised by permanganate in hot acetic acid solution; the addition of much water to the solution causes the separation of a substance, which is probably a diphenyleneimidoketone, $\text{CO}\langle\text{C}_6\text{H}_3\rangle\text{NH}$. It forms minute, yellow crystals melting at $177\text{--}179^\circ$, and is soluble in alcohol, ether, and benzene. Boiling caustic alkalis do not decompose it, and it is precipitated unchanged by water from its solution in sulphuric acid; it gives the normal molecular weight by the cryoscopic method in benzene. Potassium nitrite acts readily on its acetic acid solution, forming a *nitroso*-derivative, which is precipitated by water; it forms minute, yellow crystals melting at $128\cdot5^\circ$, is soluble in alcohol, acetic acid, ether, or benzene, and probably contains the group $\text{N}\cdot\text{NO}$. The *acetyl* derivative is obtained in long, white needles or laminæ melting at 152° . Diphenyleneimidoketone, when fused with potash, yields an *acid*, and when treated with hydroxylamine, gives a small yield of another substance; these products have not yet been investigated. The author quotes further arguments in support of the formula previously assigned by him to phenylcarbazacridine.

W. J. P.

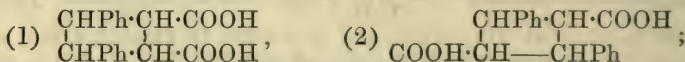
Isocarbostyryl. By A. FERNAU (*Monatsh.*, 14, 59—70).—Anhydrous isoquinoline is heated with potassium, in the form of fine wire, for 4—5 hours at 100° , and afterwards for 1 hour at $170\text{--}180^\circ$. The product is poured into a dish, and allowed to remain exposed to the air for 12—15 hours, whereby the violet-brown mass becomes a

reddish oil. The oil is dissolved in alcohol, the alcohol evaporated, and the residue mixed with water and then exhausted with ether. The ethereal solution, on evaporation, gives an oil, from which crystals of Bamberger's isocarbostyryl, $C_6H_4 < \begin{smallmatrix} CH:CH \\ | \\ CO \cdot NH \end{smallmatrix}$, separate (yield 22—25 per cent.). This compound crystallises slowly from alcohol in large, monoclinic needles; $a : b : c = 1.8500 : 1 : 1.25995$. It melts at 209° , gives a *platinochloride*, $(C_9H_7NO)_2 \cdot H_2PtCl_6$, crystallising in yellow needles, and, on distillation with zinc-dust, is again converted into isoquinoline. On heating with potassium hydroxide and methylic iodide, isocarbostyryl is converted into the *pseudomethylic salt*, C_9H_6ONMe , which melts at 54° , and does not give methylic iodide when heated with hydriodic acid. The *true methylic salt*, C_9H_6NOMe , which is obtained by treating the silver salt with methylic iodide, is an oil boiling at about 240° , and readily loses methyl when heated with hydriodic acid.

The oil, mentioned above, from which the isocarbostyryl separated, gave, on fractional distillation, a portion boiling at 233 — 235° ; but analysis did not enable the author to determine whether this consisted of *dihydroisoquinoline* or of a mixture of isoquinoline with *tetrahydroisoquinoline*. The behaviour of isoquinoline towards the alkali metals and oxygen is noteworthy, as, under like conditions, quinoline is converted into diquinolyl.

G. T. M.

Constitution of the Truxillic acids. By C. LIEBERMANN and H. SACHSE (*Ber.*, 26, 834—838; compare *Abstr.*, 1890, 1424).— β -Truxillic acid, since it yields benzile when oxidised, must be a geometrical variety of the first of the two possible structural formulæ given below, which represent the acid as a tetramethylene derivative.



and further, it must be one of those varieties in which the two COOH groups are situated on the same side of the tetramethylene ring (like phthalic acid in the benzene series), for it yields an internal anhydride, as the molecular weight of the latter, determined cryoscopically, proves; and this anhydride yields, with resorcinol, a *fluoresceïn*, $CO < \begin{smallmatrix} O \\ \parallel \end{smallmatrix} C_{16}H_{14} > C[C_6H_3(OH)_2]_2$, as an amorphous, brownish-

red powder; with aniline, an *anil*, $C_{16}H_{14} < \begin{smallmatrix} CO \\ \parallel \end{smallmatrix} > NPh$, forming colourless needles melting at 180° , and converted by cold alcoholic potash into the *anilic acid*, $COOH \cdot C_{16}H_{14} \cdot CO \cdot NPh$; this forms white crystals melting at 197° and yields a *barium salt*, $(C_{24}H_{20}NO_3)_2Ba$; with phenylhydrazine in acetic acid solution, it gives a *phenylhydrazide*, $C_{16}H_{14} < \begin{smallmatrix} CO \\ \parallel \end{smallmatrix} > N_2HPh$, forming colourless crystals melting at 218° .

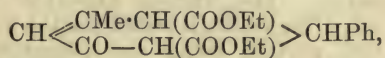
γ -Truxillic acid must have the COOH groups on opposite sides of the ring, for, although it yields an internal anhydride, this anhydride gives no fluoresceïn with resorcinol, and with aniline yields no anil,

but an *anilic acid*, forming white needles melting at 220° , together with some *anilide*, $C_6H_4(CO \cdot NPh)_2$, crystallising in needles and melting at 255° .

α -Truxillic anhydride yields no fluoresceïn, and must be an external anhydride, for its molecular weight, cryoscopically determined, corresponds with the formula $(C_{36}H_{30}O_7)_3$. C. F. B.

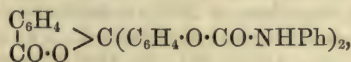
Formation of Cycloïd Compounds from 1 : 5-Diketones: Synthesis of a Structural Isomeride of Camphor. By E. KNOEVENAGEL (*Ber.*, 26, 1085—1090).—The author has employed two methods for the synthesis of 1 : 5-diketones. The first consists in the action of ethylic salts of unsaturated acids on compounds of the type of ethylic acetoacetate, and the second in heating ethylic acetoacetate with an aldehyde in the presence of a primary amine (Hantzsch). The formation of pyridine derivatives from 1 : 5-diketones and hydroxylamine, an example of which has recently been given in the case of benzamarone (this vol., i, 352), is by no means a general reaction.

Those 1 : 5-diketones which contain a methyl group in the sixth position from one of the carbonyl groups are, when treated with condensing agents, converted into derivatives of Δ_2 -ketotetrahydrobenzene (compare Hagemann, this vol., i, 393). Thus, from *ethylic deoxybenzoïmbenzalacetoacetate* and alkali there results 3 : 4 : 5-triphenyl- Δ_2 -ketotetrahydrobenzene, $CH \begin{smallmatrix} \text{CPh} \cdot \text{CHPh} \\ \text{CO} - \text{CH}_2 \end{smallmatrix} > \text{CHPh}$, which exists in two modifications, melting at 138° and 180° respectively; and when ethylic benzylidenediaceoacetate is suspended in alcohol, and treated with hydrogen chloride, the compound



which melts at 86° , is formed. The compound obtained from *ethylic isobutylidenediaceoacetate* is denominated by the author *metacamphor*, $CH \begin{smallmatrix} \text{CMe} \cdot \text{CH}_2 \\ \text{CO} - \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CHMe}_2$; it is a liquid resembling camphor and menthol in its odour, and boils at 244 — 245° (uncorr.). The corresponding derivative of the para-series may be identical with ordinary camphor. A. R. L.

Derivatives of Phenolphthaleïn and of Fluoresceïn. By A. HALLER and A. GUYOT (*Compt. rend.*, 116, 479—482).—When carefully dried phenolphthaleïn (1 mol.) is heated at 130° with phenylic isocyanate (2 mols.), *phenolphthaleïn bisphenylcarbamate*,



is obtained. It crystallises from boiling benzene in white needles which melt at 135° . It is not attacked by boiling water but when treated with alkalis, or when heated above its melting point, it yields phenolphthaleïn and symmetrical diphenylcarbamide.

Fluoresceïn bisphenylcarbamate is obtained in a similar way, and forms pale yellow, microcrystalline grains very slightly soluble in most ordinary solvents, but somewhat soluble in acetone. It melts at 195° , and splits up into fluoresceïn and phenylcarbamide.

Dibenzylphenolphthaleïn is obtained by the action of benzylic chloride on an alcoholic solution of sodiophenolphthaleïn, and crystallises from a mixture of benzene and alcohol in beautiful, blue, nacreous leaflets melting at 150° . It is only slightly soluble in boiling alcohol or in ether, but dissolves readily in benzene. When heated with alcoholic potash, it seems to be hydrolysed, but after a time the solution deposits the original compound. No oxime is formed when it is heated at 100° with hydroxylamine hydrochloride and potassium hydroxide. When an alcoholic solution of the dibenzylphenolphthaleïn is heated with zinc and hydrochloric acid, it yields a thick, transparent liquid which solidifies to a brittle, and sometimes crystalline, mass. This product is insoluble in alkalis, and when treated with acetic acid and potassium dichromate, it again yields dibenzylphenolphthaleïn.

The general properties of dibenzylphenolphthaleïn, and more particularly the fact that it yields no oxime, seem to support Baeyer's view as to the constitution of the phthaleïns.

C. H. B.

Octonaphthylene and Octonaphthenic Alcohol. By S. JU-KOFFSKY (*J. Russ. Chem. Soc.*, **24**, 201—205).—The chloride, $C_8H_{15}Cl$, boiling at 167 — 168° , obtained amongst the chlorination products of octonaphthene, was heated in a sealed tube with 1 part of dry sodium acetate and 2 parts of glacial acetic acid for 48 hours at 200° . After pouring into water and neutralising, the upper layer was separated, dried, and fractionated. The fraction 115 — 140° was distilled repeatedly over sodium, after which it boiled for the most part between 117° and 121° , this portion being the octonaphthylene already obtained by Yakoffkin. An attempt was made to prepare the hydrocarbon C_8H_{12} by the addition of 2 atoms of bromine to the octonaphthylene, and subsequent separation of $2HBr$ by heating with acetic acid and sodium acetate. No hydrocarbon, however, was obtained in this way, the product of the action boiling at a high temperature, and consisting chiefly of the ethereal salt, $CH_3 \cdot COOC_8H_{15}$; sp. gr. 0.9275 at $0^{\circ}/0^{\circ}$, b. p. 195 — 200° . From this acetate, the corresponding alcohol, $C_8H_{15} \cdot OH$, was obtained by hydrolysis, and dried by means of caustic baryta. It boils at 182.5 — 184.5° , and has the sp. gr. 0.8920 at $0^{\circ}/0^{\circ}$.

J. W.

Condensation of Metaphenylenediamine with β -Naphthol. By F. GAESS and E. ELSAESSER (*Ber.*, **26**, 976—981).—By melting the two substances together at 250° , a mixture of mono- and di- β -naphthylmetaphenylenediamine is obtained. The substance described by Ruhemann (*Abstr.*, 1882, 391) as the dinaphthyl compound is really the mononaphthyl derivative.

Mono- β -naphthylmetaphenylenediamine, $NH_2 \cdot C_6H_4 \cdot NH \cdot C_{10}H_7$, forms long, colourless needles with an asbestos-like lustre, melts at 128° , boils at about 320° under 40 mm. pressure, and exhibits in solution a

greenish-blue fluorescence; the *hydrochloride*, $C_{16}H_{14}N_2 \cdot HCl$, forms white needles which redden when kept; the *dihydrochloride* is a white powder, which is decomposed by boiling water with formation of the monochloride; both chlorides, when heated, turn red, and melt at 210° ; an alcoholic solution of the dihydrochloride fluoresces reddish-blue. The *sulphate*, $(C_{16}H_{14}N_2)_2 \cdot H_2SO_4$, crystallises in lustrous, rhombic plates, with reddish-blue fluorescence. The *picrate*, $C_{16}H_{14}N_2 \cdot C_6H_3N_3O_7$, forms golden plates melting with decomposition at 180° . The *monacetyl derivative*, $NHAc \cdot C_6H_4 \cdot NHC_{10}H_{17}$, is obtained in nodular groups of colourless needles melting at 135° , and fluorescing reddish-blue in alcoholic solution; the *diacetyl derivative*, $NHAc \cdot C_6H_4 \cdot NAc \cdot C_{10}H_7$, crystallises in bundles of colourless, non-fluorescent needles melting at $147-148^\circ$. The *benzoyl derivative*, $NHBz \cdot C_6H_4 \cdot NH \cdot C_{10}H_7$, forms large, thin, nacreous plates melting at 173° ; the *dibenzoyl derivative*, $NHBz \cdot C_6H_4 \cdot NBz \cdot C_{10}H_7$, was obtained as colourless, rhombic tables melting at 213° ; neither of these compounds fluoresces in solution.

Di-β-naphthylmetaphenylenediamine, $C_6H_4(NH \cdot C_{10}H_7)_2$, forms colourless needles, fluoresces reddish-blue in solution, melts at 192° , and boils with partial decomposition above 460° under 45 mm. pressure. The *dihydrochloride*, $C_6H_4(NH \cdot C_{10}H_7 \cdot HCl)_2$, is a white, crystalline powder which turns grey and loses hydrochloric acid when kept; it melts at 210° , turning red, and is deprived of all its hydrochloric acid by boiling with water. No picrate could be obtained. The *diacetyl derivative*, $C_6H_4(NAc \cdot C_{10}H_7)_2$, forms colourless plates melting at 175° ; the *dibenzoyl derivative*, $C_6H_4(NBz \cdot C_{10}H_7)_2$, crusts of colourless prisms melting at 215° ; neither fluoresces in solution. C. F. B.

Preparation of Naphthidine. By F. REVERDIN and C. DE LA HARPE (*Chem. Zeit.*, 16, 1687).—Naphthidine (Abstr., 1886, 245) is obtained when α -naphthylamine (100 grams) is dissolved in 88 per cent. sulphuric acid (1000 grams), ferric oxide (55 grams) added at 40° , and the mixture heated, first at 75° and subsequently at 100° , for several hours. The product is poured into water, the precipitate collected, washed with warm water, converted into base with alkali, and crystallised from alcohol. The various mother liquors appear to contain an isomeric base. The tetrazo-colours obtained by combining diazotised naphthidine with amines, phenols, &c., are feeble.

A. R. L.

Derivatives of α -Naphthylacetylene and of β -Naphthylacetylene. By J. A. LEROY (*Bull. Soc. Chim.* [3], 7, 644-649).— α -Naphthylacetylene (Abstr., 1292, 495) combines with one equivalent of sodium or potassium in the presence of ether, forming yellow, pulverulent compounds which, when suspended in anhydrous ether and treated with dry carbonic anhydride, yield the alkali salt of α -naphthylpropionic acid. The free acid crystallises from hot water or carbon bisulphide in white, silky needles which become yellowish on exposure to light, melts at $138-139^\circ$ with decomposition, and yields α -naphthylacetylene when heated with water in a sealed tube at 125° . The barium salt crystallises with 1 mol. H_2O .

α -Ethyl-naphthalene is readily chlorinated by the action of chlorine in sunlight; the portion of the product boiling at 185° (40 mm.) is the dichloro-derivative, and when this is treated with alcoholic potash at 110° , it is converted into α -naphthylacetylene.

The derivatives of β -naphthylacetylene dealt with in this paper have all been previously described (*loc. cit.*). A. R. L.

Substantive Cotton Dyes from Diamidophenanthraquinone. By S. LITTHAUER (*Ber.*, 26, 848—851).—It has been thought that meta-substituted derivatives of benzidine yield only dyes which do not dye the cotton fibre directly, but a consideration of the cases of benzidinesulphone, diamidodiphenylene oxide, and diamidocarbazole shows that this rule does not hold if the substituting groups form a ring. A further confirmation of this is obtained from the fact that diamidophenanthraquinone yields substantive dye stuffs.

Phenanthraquinonedisazoresorcinol,
$$\begin{array}{c} \text{CO} \cdot \text{C}_6\text{H}_3 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{OH})_2 \\ | \\ \text{CO} \cdot \text{C}_6\text{H}_3 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{OH})_2 \end{array}$$
, obtained by adding a diazotised solution of the diamidoquinone to resorcinol, is violet when moist, dark green and of metallic lustre when dry. *Phenanthraquinonedisazo- β -naphthol*, obtained in a similar manner from β -naphthol, is bluish-red when moist, green and metallic when dry. *Phenanthraquinonedisazo- α -naphthol*, from α -naphthol, is rather redder in colour when moist. *Phenanthraquinonedisazo- β -naphthylamine*, from β -naphthylamine, is bluish-red when moist.

C. F. B.

Action of Sulphuric acid on Menthol. By TOLOTCHKO (*J. Russ. Chem. Soc.*, 24, 249—250).—By acting in the cold with sulphuric acid on menthol, the author was unable to prepare the menthene of Walther and Beckmann, but obtained instead of it a hydrocarbon, $\text{C}_{10}\text{H}_{20}$, *mentholene*, which exhibits the properties of the polymethylenes. It boils at 168 — 169° under a pressure of 760 mm., and has the sp. gr. 0.8066 at $0^{\circ}/0^{\circ}$. Bromine is only slowly decolorised by the hydrocarbon, hydrogen bromide being evolved. A weak solution of potassium permanganate was not entirely decolorised after two weeks, although the hydrocarbon was shaken up with it daily for 8—10 hours at 50° . The action of sulphuric acid on borneol is under investigation by the author. J. W.

Camphor. By G. ODDO (*Gazzetta*, 23, i, 70—85, 85—90).—The author shows that the same camphocarboxylic acid is obtained from camphor (compare Brühl, *Abstr.*, 1892, 200), and from bromo-camphor by treatment with sodium, and subsequently with carbonic anhydride; it is quantitatively converted into bromocamphocarboxylic acid by the action of bromine on its absolute alcoholic solution (compare de Santos and Silva, *Abstr.*, 1874, 70). On boiling the bromo-acid with water, ordinary bromocamphor melting at 76° is obtained.

In an appendix to this paper, the author defends the constitutional formula previously suggested by him for camphor (*Abstr.*, 1892, 724), and criticises adversely those proposed by Brühl (*loc. cit.*), and by Collie (*Abstr.*, 1892, 864).

On adding sodium nitrite solution to camphocarboxylic acid, suspended in water, isonitrosocamphor is formed, and is then partially converted into the camphorquinone described by Claisen and Manasse (Abstr., 1889, 619). Camphocarboxylic acid should, therefore, contain the group $C_8H_{14} < \begin{smallmatrix} CH \cdot COOH. \\ CO \end{smallmatrix}$.

W. J. P.

Ethereal Salts of Camphoric acid. By J. W. BRÜHL (*Ber.*, 26, 1097—1099).—A reply to Walker (*Ber.*, 26, 600).

Derivatives of Campholenic acid. By W. THIEL (*Ber.*, 26, 922—926).—The nitrile of campholenic acid is a colourless liquid, and boils at 224° (uncorr.), and not at 216—218°, as stated by Goldschmidt and Zürrer (*Ber.*, 17, 2070). It is converted into potassium campholenate by prolonged boiling with alcoholic potash, but a pure preparation cannot be obtained unless the traces of campholenamide, which is also formed, are extracted from the aqueous alkaline solution with ether. Pure campholenic acid distils at 255—256°.

Campholene is obtained by boiling campholenic acid in a reflux apparatus. It boils at 129—130·5°. The author was unable to obtain a pure product by the distillation of calcium campholenate with soda-lime. When treated with bromine in the presence of water, hydrogen bromide is evolved and resinous products are obtained. In the absence of water, when treated with bromine in chloroform solution at -15°, it yields a *dibromide*, $C_{10}H_{16}Br_2O_2$, which melts at 96·5—97°.

Isohydroxycamphoric acid, $C_{16}H_{16}O_5$, is obtained together with acetic acid by oxidising campholenic acid with chromic acid. It crystallises from chloroform in slender needles, from water in large, vitreous prisms, melts at 129—130·5°, is bibasic, and yields easily soluble salts. It is isomeric with α -hydroxycamphoric acid (*Annalen*, 145, 212) and camphoric acid (*Annalen*, 163, 333).

Isocamphoronic acid, $C_9H_{14}O_6$, is obtained by the further oxidation of the preceding acid. It crystallises from nitric acid in large prisms, melts at 166—167°, and is tribasic.

E. C. R.

Glucosides of the Convolvulaceæ. By N. KROMER (*Chem. Centr.*, 1893, i, 310—312; from *Pharm. Rund.*, 31, 625—630, 641—646, 657—662, 673—678, 689—694, 705—712, 721—723, 737—743, 753—758, and 769—771).—Scammonin, $C_{88}H_{166}O_{42}$, the resinous glucoside of the roots of *Convolvulus scammonia*, melts at 123·68° (corr.), has $[\alpha]_D = -23\cdot06^\circ$, and is a white, amorphous powder, soluble in alcohol, ether, chloroform, &c., insoluble in light petroleum and water. It is an acid anhydride, and by the action of alkalis is hydrolysed into the bibasic *scammonic acid*, $C_{22}H_{44}O_{13}$, an amorphous, yellow substance of strongly acid reaction, which decomposes carbonates.

Scammonin is oxidised by nitric acid into oxalic, valeric, and butyric acids, carbonic anhydride, and an acid melting at 101°, which is isomeric with sebacic acid. Potassium permanganate oxidises

scammonin to oxalic and valeric acids, and the monobasic *scammonolic acid*, $C_{16}H_{30}O_3$, which forms a wavellite-like mass melting at 65.8° . When hydrolysed with mineral acids, scammonin yields *scammonole*, $C_{16}H_{30}O_3 + \frac{1}{2}H_2O$ (2 mols.), which melts at $63-77^\circ$, valeric acid (4 mols.), and a sugar (6 mols.), which is closely related to mannose; the latter is fermentable, does not crystallise, and has a rotatory power of $+17.78^\circ$ at 19° . 0.00763 gram of the sugar reduces 1 c.c. of Fehling's solution. The *pentabenzoyl* compound, $C_6H_7O_6Bz_5$, is a white powder, and melts at 63° ; the phenylhydrazine compound, forms clear, yellow needles, and melts at 191° .

Turpethin, $C_{76}H_{128}O_{36}$, the glucoside of the roots of *Ipomœa turpethum*, is an amorphous, yellow powder, colourless in thin layers, and melts at 146.8° (corr.); it has a rotatory power of -30.14° , and is sparingly soluble in chloroform, soluble in alcohol and acetic acid. When treated with alkalis, it yields *turpethic acid*, a yellow, hygroscopic mass. By oxidation with nitric acid, turpethin yields oxalic, isobutyric, and sebacic acids and carbonic anhydride, whilst potassium permanganate oxidises it to oxalic, isobutyric, and turpetholic acids. When hydrolysed with mineral acids, it yields isobutyric acid (1 mol.), *turpethole*, $C_{16}H_{30}O$ (? $C_{16}H_{30}O_3$), a substance forming feathery, interlaced crystals, and melting at 85.76° (1 mol.), glucose (3 mols.), and a viscid, liquid acid, which was not isolated but gave a silver salt, $C_{15}H_{27}O_5Ag$.

Turpetholic acid, $C_{16}H_{32}O_4$, is obtained, as above mentioned, and also by the action of alkalis or their carbonates on turpethole. It forms a hard, white, crystalline mass, melts at 88.4° , and is soluble in alcohol, sparingly soluble in ether; turpethole seems to be the anhydride of turpetholic acid.

A. J. G.

Active Principles of Bryony Root. By MASSON (*J. Pharm.* [5], 27, 300—307).—Bryony root is extracted with cold 3 per cent. hydrochloric acid, the extract precipitated by tannin, the purified precipitate extracted with alcohol, and the bryonin liberated in an impure state by zinc oxide. It is purified by dissolving it in hydrochloric acid, removing the acid by dialysis, drying the residue, dissolving in alcohol, and precipitating the pure substance with ether.

Bryonin, $C_{34}H_{48}O_9$, is a white, very bitter, amorphous powder, and dextrorotatory, $[\alpha]_D = +41.25^\circ$. It is precipitated by tannin and ammoniacal lead acetate, and is hydrolysed by dilute sulphuric acid into glucose and a resinous substance, *bryogenin*, $C_{14}H_{19}O_2$, which melts at 210° , and is dextrorotatory, $[\alpha]_D = +105^\circ$. This dissolves in concentrated sulphuric acid to a red solution, which changes to purple on heating, and from which a purple precipitate is then obtained on the addition of water. The residue left after extracting the root with water yields a resin on further extraction with alcohol. *Bryoresin*, $C_{37}H_{68}O_{18}$, is a red, amorphous substance which softens at 15° , but becomes liquid only at 250° . It forms compounds with alkalis, lead, and copper.

JN. W.

Saponins. By R. KOBERT (*Chem. Centr.*, 1893, i, 32, 33; from *Pharm. Post*, 25, 1141—1144, 1168—1171; compare Abstr., 1891,

1532). A large number of glucosides are comprehended under the name of saponin substances, and are characterised by the properties that their aqueous solutions froth strongly, that they prevent the deposition of finely-divided precipitates, &c. Chemically, they belong to several series, but those of the general formulæ $C_nH_{2n-8}O_{10}$ are especially numerous, and of these the following list is given:— $C_{17}H_{26}O_{10}$: Saponin, senegin, Quillaja-sapotoxin, Sapindus-sapotoxin, Gypsophila-sapotoxin, Agrostemma-sapotoxin. $C_{18}H_{28}O_{10}$: Saponin II, digitonin (Schmiedeberg), saporubin, senegin, assamin. $C_{19}H_{30}O_{10}$: Saponin III, quillajic acid, polygalic acid, Herniaria-saponin. $C_{20}H_{32}O_{10}$: Cyclamin, digitonin (Paschke), Merck's quillajic acid, Sarsaparilla-saponin. $C_{22}H_{36}O_{10}$: Sarsasaponin. $C_{26}H_{44}O_{10}$: Parillin. $C_{26}H_{50}O_{10}$: Melanthin. There is some doubt as to whether certain of these substances really belong to this series, but it is probable that dulcamarin, $C_{22}H_{31}O_{10}$, and syringin, $C_{17}H_{26}O_{10}$, will on further investigation be found to do so. Some other glucosides of quite different composition, for instance, paridin, $C_{16}H_{28}O_7$, judged by their properties, belong to the saponin substances.

The original paper contains a classified list of the plants, 140 in number, in which saponin substances have been detected.

A. J. G.

Action of Phosphoric Chloride on Santonin. By J. KLEIN (*Ber.*, 26, 982—983).—The product of the action of phosphoric chloride on santonin has not the formula $C_{15}H_{16}OCl_2$ (this vol., i, 112), but $C_{15}H_{15}Cl_3O_2$; the third chlorine atom seems to be in the ring. The substance melts with decomposition at 171—172°, and yields a hydrazone with phenylhydrazine; it has the properties of an unsaturated compound. The facts favour the conclusion that santonin is a δ -lactone, and contains two carbon atoms which are capable of forming a double bond between them, which double bond is probably in the lactone ring.

C. F. B.

Derivatives of Santonin. By J. KLEIN (*Ber.*, 26, 1069—1071).—A reply to Cannizzaro (this vol., i, 364).

Fumaroid and Maleinoid Structure of some Derivatives of Santonins. By G. GRASSI-CRISTALDI (*Gazzetta*, 23, i, 65—69).—The author considers that santononic and isosantononic acids or santonone and isosantonone, are respectively fumaroid and maleinoid isomerides; he is still engaged on experimental work in connection with this subject.

W. J. P.

Action of Hydrochloric acid on the Santonones. Bisdihydrosantoninic acid. By G. GRASSI-CRISTALDI (*Gazzetta*, 23, i, 58—65; compare *Abstr.*, 1892, 869; this vol., i, 110).—*Methylic bisdihydrosantoninate*, $C_{32}H_{38}O_4$, is prepared by passing hydrogen chloride through a solution of santonone or isosantonone in methyl alcohol; after purification, the salt is obtained in colourless, thin needles melting at 131°; it is soluble in alcohol, ether, benzene, ethylic acetate, and chloroform, sparingly so in light petroleum. It has a specific rota-

tion $[\alpha]_D = +97.1^\circ$ in a 2.65 per cent. benzene solution at 24° , and has a normal molecular weight in freezing benzene or acetic acid.

Bisdihydrosantinic acid, $C_2 \left(\begin{array}{c} \text{CMe} = \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH} \cdot \text{CMe} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{CHMe} \cdot \text{COOH} \end{array} \right)_2$, is obtained by boiling its methylic salt with alcoholic baryta, adding hydrochloric acid, and crystallising the precipitated acid from alcohol; it forms colourless, silky needles melting at 215° , and has a specific rotatory power $[\alpha]_D = +34.9^\circ$ in a 1.65 per cent. acetic acid solution at 24° . The acid is sparingly soluble in alcohol, glacial acetic acid, benzene, or ether; it is insoluble in carbonates or caustic alkalis in the cold, and its salts are decomposed by passing a current of carbonic anhydride through their solutions. Nearly all the salts are insoluble in water, with the exception of those of the alkali metals.

W. J. P.

Methylbrazilin. By J. HERZIG (*Monatsh.*, 14, 56—58).—Methylbrazilin, which melts at 137 — 138° , proves to be a trimethyl compound having the formula $C_{16}H_{19}O_5Me_3$, and not a tetramethyl compound, as stated by Schall and Dralle (compare Abstr., 1888, 295; 1889, 55, 1004).

G. T. M.

Constitution of Five-membered Rings. By E. BAMBERGER (*Annalen*, 273, 373—379).—A reply to Ciamician and Hinsberg.

F. S. K.

Synthesis of Oxypyridine and Oxypiperidine Bases. By A. LADENBURG (*Ber.*, 26, 1060—1069; compare Abstr., 1890, 67; 1891, 1092).—The author has prepared 1-methylpipercolylalkine from pure picoline, and confirms the physical constants previously given by him for it and its derivatives, so that Lipp's compound (Abstr., 1891, 1245) was, perhaps, a stereoisomeride.

1-Methylvinylpiperidine, $C_8H_{11}Me \cdot C_2H_3$, is obtained by gradually adding concentrated sulphuric acid in the cold to a solution of hydrotropine in glacial acetic acid and heating the mixture at 190° . It is a colourless liquid having the odour of coniine and tropidine, boils at 159 — 162° , and is soluble in an equal volume of water; the platinum-chloride melts at 197 — 198° .

The author has failed to obtain tropine by the oxidation of hydrotropine with various reagents. When an aqueous solution of hydrotropine is boiled with chloranil, a base is produced giving an aurochloride and mercuriochloride differing only in melting point from those of tropine; whilst by oxidising benzoylhydrotropine with hydrogen peroxide and boiling the product with potash, a similar base is obtained yielding a mercuriochloride melting at 210° , an aurochloride melting at 180° , and a crystalline methochloride. This base, which may be a mixture of tropine and hydrotropine, is provisionally named *α-tropine*; it yields a compound (*α-homatropine*) with mandelic acid, having mydriatic properties. The author contends that, although he has failed to synthesise tropine, the last-described base so closely resembles that compound in its properties, that the experiments may be taken as a confirmation of his previously published views on the constitution of tropine.

The remainder of the paper is polemical, and the author upholds his formulæ against those proposed by Merlin (Abstr., 1892, 359), which he regards as based on fictitious evidence. He is able to agree with Merlin in regard to the constitution of one compound only, namely, that of tropilidene. A. R. L.

Resolution of β -Pipicoline into its Optical Isomerides. By A. LADENBURG (*Ber.*, 26, 1069).—Experiments, which are still in progress, have proved that β -pipicoline may be resolved into its optical isomerides by crystallising its tartrate (compare this vol., i, 442). A. R. L.

Penthiazolines. By G. PINKUS (*Ber.*, 26, 1077—1084).—Penthiazolines are obtained more readily from thiamides and trimethylene chlorobromide than when trimethylene bromide is used, probably on account of the lower melting point of the former.

Mesophenylpenthiazoline, $\text{CPh} \begin{smallmatrix} \text{S} \cdot \text{CH}_2 \\ \text{N} \cdot \text{CH}_2 \end{smallmatrix} > \text{CH}_2$, is obtained by heating together thiobenzamide and trimethylene chlorobromide. It crystallises from water in small, white needles, melts at 44—45°, is volatile with steam, but cannot be distilled alone without decomposition. The *platinochloride* melts at 185°, and the *mercurochloride* at 140—142°. When heated in a sealed tube with hydrochloric acid at 200—210°, it yields benzoic acid and amidopropyl mercaptan, together with hydrogen sulphide; whilst homotaurine and its benzoyl derivative are formed when it is heated on the water-bath with bromine water. The *methiodide*, $\text{C}_{10}\text{H}_{11}\text{NS} \cdot \text{MeI}$, is obtained by treating the new base with methylic iodide; it melts at 184°, is decomposed by hydrochloric acid and bromine water in a manner analogous to the parent compound, yields an oily compound, $\text{C}_{22}\text{H}_{28}\text{N}_2\text{S}_2\text{O}_2$, on treatment with alkali, and when shaken with moist silver chloride, the *methochloride* is formed, the *platinochloride* of which melts at 191°.

Mesorthotolylpenthiazoline is an oil, and *mesoparatolylpenthiazoline* melts at 52—53°.

Mesobenzylpenthiazoline, prepared from phenylacetic thiamide and trimethylene chlorobromide, is a liquid of sp. gr. 1.113 at 15°, having an odour resembling that of hemlock.

Mesomethylpenthiazoline is obtained from thiacetamide and trimethylene chlorobromide; the yield is poor. It is a colourless liquid miscible with water, boils at 173° (757 mm.); the *picrate* melts at 138°. Mesomethylthiazoline (Abstr., 1891, 816) can be prepared from thiacetamide and ethylene dibromide.

A compound, $\text{C}_8\text{H}_{16}\text{ClBrN}_2\text{S}_2\text{O}_2$, melting at 102—103° is obtained by heating xanthogenamide, $\text{OEt} \cdot \text{CS} \cdot \text{NH}_2$, with trimethylene chlorobromide. A. R. L.

Formation of Isoquinoline. By E. FISCHER (*Ber.*, 26, 764—765; compare P. Fritsch, this vol., i, 366).—Benzoylacetalamine hydrochloride is dissolved in fuming sulphuric acid, and the dark-red solution allowed to remain for 24 hours; on dilution and neutralisation, isoquinoline is obtained; it was identified by means of the

platinochloride. With concentrated sulphuric acid, the aldehyde yields a base which is volatile with steam, and is probably a hydroisoquinoline.

Benzoylacetalamine, on treatment with fuming sulphuric acid, also yields a crystalline condensation product which is being further investigated.

J. B. T.

Triphenylpiperazine. By L. GARZINO (*Gazzetta*, **23**, i, 9—20; compare Abstr., 1892, 633).—The author gives a new method for preparing triphenyltetrahydropyrazine by which a good yield (83 per cent.) may be obtained and the formation of diphenylpiperazine avoided. The former substance melts at 130—131°, boils above 360° under 240 mm. pressure, and crystallises in the orthorhombic system, $a:b:c = 0.7657:1:1.8624$; its benzene and ethereal solutions show an intense blue fluorescence. On reduction with tin and hydrochloric acid, triphenyltetrahydropyrazine yields ethylenediphenyldiamine and acetophenone; this is the result of simultaneous hydrolysis and reduction, and is the first recorded case in which the nitrogen ring has been broken, yielding the substances from which the condensation product was originally formed. Triphenyltetrahydropyrazine, dissolved in absolute alcohol, is reduced by sodium with formation of *triphenylpiperazine*, $\text{NPh} < \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHPh} \end{smallmatrix} > \text{NPh}$; this base is obtained in small needles melting at 101—102°, and its solution in benzene, ether, or light petroleum shows a blue fluorescence. It dissolves in mineral acids and is precipitated unchanged by water; it does not reduce metallic salts or yield definite double salts. The *picrate* forms small, yellow crystals melting at 173—175°. The *platinochloride*, $\text{C}_{22}\text{H}_{22}\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$, is obtained in minute, yellow crystals which decompose at about 220°; it is insoluble in ether or water, but dissolves in alcohol. An ethereal solution of triphenylpiperazine absorbs the quantity of bromine necessary to form a mono-substitution derivative; one half of the liberated hydrogen bromide is retained by the solution.

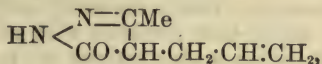
W. J. P.

Pyrazolone. By R. v. ROTHENBURG (*Ber.*, **26**, 868—872; compare this vol., i, 367, 368).—The preparation of pure pyrazolone from the carboxylic acid is attended with considerable difficulty owing to the smallness of the yield; it was finally obtained as a colourless oil which boils at 152—157°, and is fairly stable towards light; the darkening sometimes observed is probably due to the presence of a small quantity of impurity, which boils at 203—205°, and may consist of *dipyrazolone ketone*. The vapour density of pyrazolone, obtained by Victor Meyer's method, confirmed the formula $\text{C}_3\text{H}_4\text{N}_2\text{O}$. The derivatives have only been obtained in small quantities; 4-*is*-nitrosopyrazolone is a reddish-yellow oil, which crystallises in the cold, 4-*azobenzenep*pyrazolone is also red and has acid properties, and 4-*benzalpy*razolone has likewise a red colour. *Pyrazolonaldehyde*, $\text{CO} < \begin{smallmatrix} \text{NH} \cdot \text{N} \\ \text{CH}_2 \cdot \text{C} \end{smallmatrix} \cdot \text{CHO}$, is obtained by distilling calcium pyrazolonecarboxylate with lime and calcium formate; it passes over as a yellow oil

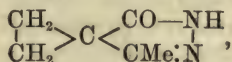
which quickly crystallises, and has all the usual properties of an aldehyde.

The author has investigated the action of hydrazine hydrate on ethylic oxalodiacetate, in the hope of obtaining bispirazolone, but the reaction proceeds in the same manner as with other orthodiketones. The ethylic oxalodiacetate, $C_2O_2(CH_2 \cdot COOEt)_2$, was obtained from the residues from the preparation of ethylic oxalacetate, and was found by the author to crystallise from dilute alcohol in flat needles melting at $82-83^\circ$. It reacts violently with hydrazine hydrate forming ethylic β -hydrazo- β_1 -ketadipate,
$$\begin{array}{c} \text{NH} \\ | \\ \text{NH} > \text{C} < \begin{array}{l} \text{CH}_2 \cdot \text{COOEt} \\ \text{CO} \cdot \text{CH}_2 \cdot \text{COOEt} \end{array} \end{array}$$
 which crystallises from very dilute alcohol in brownish-yellow needles, melts at 93° , and yields hydrazine sulphate on boiling with dilute sulphuric acid.

Hydrazine hydrate acts on ethylic allylacetoacetate in the normal manner yielding 3-methyl-4-allylpirazolone,



which crystallises from alcohol in plates, melts at 195° , shows the characteristic reactions of the pyrazolones, and like all the 3:4-derivatives gives an intense reddish-brown coloration with ferric chloride. The hydrate also combines readily with ethylic acetyltrimethylene-carboxylate yielding 3-methyl-4-trimethylenepirazolone,



which crystallises in almost colourless needles, melts at 195° , and gives the characteristic brown coloration with ferric chloride, but does not combine with diazobenzene chloride and nitrous acid.

H. G. C.

Synthesis of Pyrazole Derivatives by means of Ethylic Diazoacetate. By E. BUCHNER (*Annalen*, 273, 214—231).—The compounds formed by the combination of ethereal salts of unsaturated acids with those of diazoacetic acid are derivatives of pyrazole. Methylic acetylenedicarboxylate, for example, combines with methylic diazoacetate forming in all probability an unstable compound of the constitution
$$\begin{array}{c} \text{COOMe} \cdot \text{C} - \text{CH} \cdot \text{COOMe} \\ | \qquad \qquad | \\ \text{COOMe} \cdot \text{C} \cdot \text{N} \cdot \text{N} \end{array}$$
 which then undergoes intramolecular change into methylic pyrazoletricarboxylate,

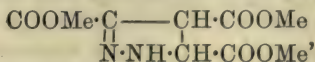


Other acetylenic ethereal salts, methylic phenylpropiolate, for example, behave in a similar manner, but ethylenic derivatives such as the ethereal salts of acrylic, fumaric, maleic, aconitic, itaconic, citraconic, cinnamic, and benzalacetic acids yield reduction products of pyrazole or pyrazoline derivatives. Methylic fumarate and methylic diazoacetate,

for instance, may be assumed to combine to form methylic psuedo-pyrazolinetricarboxylate,

$$\begin{array}{c} \text{COOMe} \cdot \text{CH} \cdot \text{CH} \cdot \text{COOMe} \\ | \quad | \\ \text{N} : \text{N} \cdot \text{CH} \cdot \text{COOMe} \end{array}$$

which is immediately converted into methylic pyrazolinetricarboxylate,



by intramolecular change.

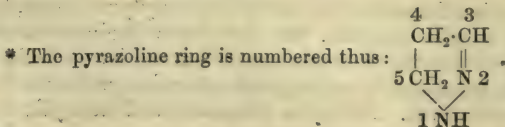
The pyrazole nucleus, like that of benzene, is extremely stable, probably owing to the existence of central linkings; its constitution may therefore be represented in the manner shown above in order to express the difference in behaviour between pyrazole and pyrroline. Pyrazoline derivatives, on the other hand, behave like fatty substances, so that the nucleus may be represented as unsaturated in the ordinary manner.

Ethereal salts of halogen-substituted acids, such as those of bromomaleïc, α -bromocinnamic, β -iodopropionic, $\alpha\beta$ -dibromopropionic, and $\alpha\beta$ -dibromosuccinic acids, also combine with ethereal salts of diazoacetic acid yielding halogen derivatives of pyrazoline, which are extremely unstable, being converted into pyrazole derivatives with elimination of a halogen acid.

The most important reactions of pyrazoline derivatives are the following:—The silver salts of the pyrazolinecarboxylic acids are converted into silver, carbonic anhydride, and pyrazole when heated in a stream of carbonic anhydride. When the acids are carefully oxidised, they are converted into pyrazolecarboxylic acids, but at the same time carbonic anhydride is eliminated, so that a mixture of acids is obtained. Ethereal salts of pyrazolinecarboxylic acids are readily converted into the corresponding pyrazole derivatives on treatment with bromine, the substitution product first formed being decomposed with liberation of hydrogen bromide. On reduction, the pyrazoline derivatives are converted into pyrazolidine derivatives.

The extreme instability of the pyrazoline nucleus is strikingly illustrated by the readiness with which the ethereal salts of the pyrazolinecarboxylic acids are converted into trimethylene derivatives with evolution of nitrogen (compare Abstr., 1888, 1274; 1890, 736; 1892, 849); pyrazoline derivatives are also unstable towards boiling mineral acids, being generally converted into hydrazine, carbonic anhydride, and products of unknown composition. F. S. K.

Pyrazoline-3:5-dicarboxylic acid. By E. BUCHNER and A. PAPENDIECK (*Annalen*, 273, 232—238; compare Abstr., 1890, 736).—Methylic pyrazoline-3:5-dicarboxylate,* $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_4$, is formed when methylic acrylate is carefully treated with methylic diazoacetate, care being taken that the temperature of the mixture does not rise above



50° or so; when a mixture of the two ethereal salts is heated immediately on the water-bath, explosive combination ensues. It crystallises well from boiling methyl alcohol and hot water, melts at 94°, and is decomposed by boiling dilute sulphuric acid with formation of carbonic anhydride and hydrazine; when treated with bromine in chloroform solution, it is converted into methylic pyrazole-dicarboxylate, melting at 151·5° (see below). The *silver* derivative, $C_7H_8N_2O_4Ag$, is a yellowish-brown powder.

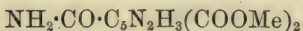
Pyrazoline-3 : 5-dicarboxylic acid, $C_5H_6N_2O_4$, is formed when the methylic salt is hydrolysed with cold methyl alcoholic potash; it crystallises in colourless prisms, turns brown at 240°, and melts at 242°, with complete decomposition. On oxidation with sulphuric acid and freshly precipitated manganese dioxide, it yields a pyrazolecarboxylic acid, melting at 208—210°, and pyrazole-3 : 5-dicarboxylic acid. The *silver* salt is a colourless compound, stable in the light, and only sparingly soluble in boiling water. The *barium* salt and the *copper* salt are readily soluble. When the silver salt is heated in a stream of carbonic anhydride, it yields pyrazole, melting at 70° (compare Abstr., 1889, 1214).

Ethylic pyrazolinedicarboxylate, $C_9H_{14}N_2O_4$, is formed, together with ethylic iodacetate, when ethylic β -iodopropionate is heated with ethylic diazoacetate (2 mols.) at 100—110°, nitrogen being evolved; it crystallises in colourless, lustrous prisms, and melts at 99°.

F. S. K.

Pyrazoline-3 : 4 : 5-tricarboxylic acid. By E. BUCHNER and H. WITTER (*Annalen*, 273, 239—245; compare Abstr., 1888, 1274).—Methylic pyrazoline-3 : 4 : 5-tricarboxylate (methylic fumaricdiazoacetate), $C_9H_{12}N_2O_6$, is formed when methylic fumarate or methylic maleate is warmed with methylic diazoacetate in light petroleum solution; it separates from ether in crystals, melts at 61°, and is very readily soluble in most ordinary solvents. It is immediately oxidised by potassium permanganate in alkaline solution, and when boiled with mineral acids, it is decomposed into hydrazine, carbonic anhydride, and other compounds. The *silver* derivative is a yellowish, very unstable substance, soluble in ammonia.

Pyrazoline-3 : 4 : 5-tricarboxylic acid, $C_6H_6N_2O_6$, crystallises in almost colourless needles, has no definite melting point, and is hygroscopic and very unstable. The *barium* salt, $(C_6H_3N_2O_6)_2Ba_3$, and the *silver* salt, $C_6H_3N_2O_6Ag_3$, were prepared; the latter yields pyrazole on dry distillation. The *amide*, $C_6H_9N_5O_3$, prepared by treating the methylic salt with alcoholic ammonia, is a crystalline compound, and decomposes at about 230°. When diazoacetamide is heated with methylic fumarate at 70°, an amide of the composition



is formed; it separates from alcohol in almost colourless crystals, and melts at about 108°.

F. S. K.

Pyrazole-3 : 5-dicarboxylic acid. By E. BUCHNER and A. PAENDIECK (*Annalen*, 273, 246—251).—*Methylic pyrazole-3 : 5-dicarboxylate*, $C_7H_8N_2O_4$, is obtained, together with methylic brom-

acetate, when methylic $\alpha\beta$ -dibromopropionate is heated with methylic diazoacetate. It crystallises in lustrous plates, melts at 151.5° , gives a stable, colourless silver derivative, and is not oxidised by potassium permanganate in alkaline solution. The corresponding acid, $C_5H_4N_2O_4$, separates from hot water in crystals containing $1H_2O$, and melts at $287-290^\circ$ with decomposition; it is extremely stable, and is not acted on by potassium permanganate. The acid sodium salt, $C_5H_3N_2O_4Na, C_5H_4N_2O_4$, is precipitated when a neutral solution of the sodium salt is treated with a solution of the acid; it crystallises with $11H_2O$, all of which are expelled at 150° . The calcium salt, $C_5H_2N_2O_4Ca + 5H_2O$, forms small, lustrous crystals, and loses its water at 200° . The barium salt, with $4H_2O$, forms lustrous prisms, and loses its water at 180° . The silver salt, $C_5H_2N_2O_4Ag_2$, is readily soluble in ammonia; on dry distillation, it yields pyrazole.

F. S. K.

Pyrazole-3:4:5-tricarboxylic acid. By E. BUCHNER and M. FRITSCH (*Annalen*, **273**, 252—256).—When methylic pyrazole-3:4:5-tricarboxylate (methylic acetylenedicarboxylodiazooacetate, Abstr., 1889, 694) is treated with concentrated nitric acid, it is converted into the corresponding acid (acetylenedicarboxylodiazooacetic acid); the latter, on rapid distillation, is converted into pyrazole and pyrazole-4-carboxylic acid, $C_4H_4N_2O_2$, a yellowish, crystalline compound melting at 275° with decomposition.

Methylic pyrazole-3:4:5-tricarboxylate is formed, together with methylic bromacetate, by the action of methylic diazoacetate on methylic bromomaleinate; it can also be obtained by treating the diazo-compound with methylic dibromosuccinate.

F. S. K.

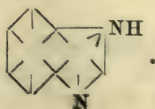
Preparation and Derivatives of Pyrazole. By E. BUCHNER and M. FRITSCH (*Annalen*, **273**, 256—266; compare Abstr., 1889, 1214).—Bromopyrazole melts at $96-97^\circ$, not at $87-88^\circ$, as previously stated; its nitrate, $C_3H_3N_2Br, HNO_3$, separates from boiling water in crystals melting at $184-185^\circ$ with decomposition; its silver derivative has the composition $C_3H_2N_2BrAg$.

Iodopyrazole, $C_3H_3N_2I$, prepared by treating the silver derivative of pyrazole with an ethereal solution of iodine, crystallises in colourless needles, melts at 108.5° , and forms a colourless silver derivative.

Nitropyrazole, $C_3H_3N_3O_2$, is formed when pyrazole is heated at 100° with a mixture of fuming nitric acid and anhydrosulphuric acid; it crystallises in colourless needles, melts at 162° , and explodes slightly when heated on platinum foil.

F. S. K.

Imidazoles. By E. BAMBERGER (*Annalen*, **273**, 267—269).—The author regards the benzimidazoles as hexacentric compounds, and represents the nitrogen atom of the imido-group as being pentavalent, the other trivalent, as shown in the formula

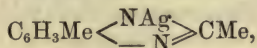


According to this view, the basicity of the imidazoles is independent of the imido-group, which, being saturated, cannot form additive products with acids. The experiments described in the following papers were undertaken with the object of settling the constitution of the benzimidazoles and of elucidating their methods of formation.

F. S. K.

Constitution and Formation of Benzimidazoles. By E. BAMBERGER and J. LORENZEN (*Annalen*, **273**, 269—302; compare Abstr., 1892, 631 and 632).—The facts which point to the conclusion that the two nitrogen atoms in the benzimidazoles have different functions are the following:—Although the benzimidazoles contain two atoms of nitrogen, they form additive compounds with only one molecule of a monobasic acid and with only one molecule of an alkyl halogen compound. The imido-group has an acid character, and imparts to some benzimidazoles the character of a phenol, to others that of an acid; all secondary benzimidazoles contain one hydrogen atom which can be displaced by metals, and they are as a rule soluble in alkalis. The benzimidazoles do not yield nitroso-derivatives as would be expected if they contained an ordinary imido-group in which the nitrogen is trivalent; their acetyl derivatives are very unstable, and are quickly decomposed by boiling water. The imido-group in the glyoxalines has the same character as that in the benzimidazoles, but in the dihydroglyoxalines it has quite different functions.

Silver derivatives of the benzimidazoles, such as



can be prepared by treating an alcoholic solution of the base first with ammonia and then with silver nitrate; they are colourless compounds, practically insoluble in water, ammonia, and organic solvents. Of the corresponding sodium derivatives, only that of 2:2'-dimethylbenzimidazole was analysed; it crystallises in slender needles, and is decomposed by water, whereas the corresponding derivatives of the other benzimidazoles are stable in aqueous solution.

2:2':3'-Trimethylbenzimidazole, $\text{C}_{10}\text{H}_{12}\text{N}_2$, is formed in small quantities when the sodium or silver derivative of 2:2'-dimethylbenzimidazole is treated with methylic iodide in methyl alcoholic solution, but it is best prepared from the base itself; it crystallises in lustrous prisms, melts at 141—142°, and is identical with the compound obtained by Niementowski (*Ber.*, **20**, 1878) from methylnitroparacetotoluidide, a fact which explains the mechanism of the benzimidazole formation.

2:2'-Dimethyl-3'-benzylbenzimidazole, $\text{C}_{16}\text{H}_{16}\text{N}_2$, prepared in a similar manner, crystallises in long, lustrous needles, and melts at 144°; the platinochloride, $(\text{C}_{16}\text{H}_{16}\text{N}_2)_2, \text{H}_2\text{PtCl}_6$, crystallises in transparent, lustrous plates.

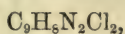
Ethylic 2:2'-dimethylbenzimidazole-3'-acetate, $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_2$, is formed when dimethylbenzimidazole is treated with sodium ethoxide and ethylic chloracetate in alcoholic solution; it crystallises in slender lustrous needles, and melts at 130·5°.

2:2'-Dimethyl-3'-acetylbenzimidazole, $C_{11}H_{12}N_2O$, can be obtained by heating the silver derivative with a benzene solution of acetic chloride; it crystallises in lustrous needles, melts at $241-242^\circ$, and is quickly decomposed by boiling water. The *platinochloride*, $(C_{11}H_{12}N_2O)_2, H_2PtCl_6$, crystallises in golden needles.

2:2'-Dimethyl-3'-chlorobenzimidazole (chlorimide), $C_9H_8N_2Cl$, is precipitated in slender needles when a saturated solution of bleaching powder is added to a well-cooled solution of 2:2'-dimethylbenzimidazole in dilute acetic acid; the crude product melts at 92° , and is insoluble in water. In its warm alcoholic solution, aniline produces a red coloration which changes to bluish-violet on adding hydrochloric acid; its aqueous solution oxidises quinol to quinhydrone. The moist substance slowly undergoes decomposition even in the cold, more quickly when warmed or when treated with hydrochloric acid, being partly converted into dimethylbenzimidazole with evolution of chlorine, partly into the isomeride described below.

Chloro-2:2'-dimethylbenzimidazole, $C_9H_8N_2Cl$, is best prepared by boiling the preceding compound with dry benzene, as, under these conditions, the formation of other products is almost entirely prevented; it crystallises in short, lustrous needles, melts at 223° , and is soluble in soda. The *hydrochloride*, $C_9H_8N_2Cl, HCl$, crystallises in long needles. The *platinochloride*, $(C_9H_8N_2Cl)_2, H_2PtCl_6$, forms golden needles, and is sparingly soluble in water. The *picrate*, *ferrocyanide*, and *nitrate* are crystalline, sparingly soluble compounds. The *silver* derivative has the composition $C_9H_8N_2ClAg$.

Chloro-2:2'-dimethylchlorobenzimidazole (chlorochlorimide),



is precipitated in yellowish needles when the preceding compound is treated with bleaching powder under the conditions already described, the hydrogen of the imido-group being substituted; the crude product melts at 85° , but after recrystallisation from alcohol and water at $103-105^\circ$. It is moderately stable when dry, but the moist substance undergoes decomposition at the ordinary temperature with evolution of chlorine, especially when treated with hydrochloric acid; when boiled with dry benzene, it seems to yield a mixture of chlorodimethylbenzimidazole (m. p. 223°), a dichlorinated derivative, $C_9H_6N_2Cl_2$, melting at 238° , and a trichlorinated derivative melting at about 285° .

Dichloro-2:2'-dimethylchlorobenzimidazole (dichlorochlorimide) is formed when the dichloro-compound melting at 238° is treated with bleaching powder solution; the crude product melts at 120° with decomposition, is decomposed by acids with evolution of chlorine, and undergoes intramolecular change into the trichloro-compound described below when boiled with alcoholic benzene.

Trichloro-2:2'-dimethylbenzimidazole, $C_9H_7N_2Cl_3$, is best prepared by treating dimethylbenzimidazole with bleaching powder in boiling hydrochloric acid solution; it is soluble in acids and alkalis, and its solution in alcoholic ammonia gives with silver nitrate a colourless, amorphous precipitate of the composition $C_9H_6N_2Cl_3Ag$. The *hydrochloride*, $C_9H_7N_2Cl_3, HCl$, crystallises in lustrous plates; the *platino-*

chloride, $(C_9H_7N_2Cl_3)_2 \cdot H_2PtCl_6$, in long needles; the *nitrate* and the *sulphate* are also crystalline.

These salts are decomposed by water, being converted into transparent gelatinous masses, but, on heating gently, the base separates in small, lustrous prisms.

Trichloro-2:2'-dimethylchlorobenzimidazole, $C_9H_6N_2Cl_4$, is formed when the preceding compound is treated with bleaching powder in cold dilute hydrochloric acid solution; it is a crystalline powder, does not melt at 310° , and is decomposed by water, alcohol, and mineral acids with evolution of chlorine, being reconverted into the trichloro-compound.

The amidines resemble the benzimidazoles in constitution, and, like the latter, they have the property of forming silver derivatives; the compound, $C_{14}H_{12}N_2Ag$, prepared from ethenyldiphenylamidine is insoluble in water, ammonia, and alcohol, and is not decomposed by boiling with water or hot dilute alcohol, whereas with boiling absolute alcohol it gives a silver mirror. Ethenyldiphenylamidine resembles the 2-methylbenzimidazole derivative in combining with phthalic anhydride to form a yellow, crystalline dye, which, however, could not be separated from the phthalanil produced at the same time; methenyldiphenylamidine, on the other hand, does not yield a trace of a yellow compound when heated with phthalic anhydride.

F. S. K.

Behaviour of the 2'-Methyl Group in Benzimidazoles. By E. BAMBERGER and B. BERLÉ (*Annalen*, **273**, 303—342; compare *Abstr.*, 1892, 631 and 632).—*Benzylidenedimethylbenzimidazole*,



is formed when 2:2'-dimethylbenzimidazole is heated with benzaldehyde at 200° ; it is a colourless, flocculent substance, sinters at about 100° , and melts at about 120° with effervescence. The *hydrochloride*, $C_{16}H_{14}N_2 \cdot HCl$, crystallises in colourless needles, melts at 283 — 284° , and is readily soluble in alcohol, but very sparingly in water; the anhydrous salt is hygroscopic. The *platinochloride*, $(C_{16}H_{14}N_2)_2 \cdot H_2PtCl_6$, is a yellow, crystalline powder. The *dibromide* crystallises in yellowish needles, and has no definite melting point.

The *phthalone*, $C_{17}H_{12}N_2O_2$, prepared by heating 2:2'-dimethylbenzimidazole with phthalic anhydride at 200° , crystallises in yellow, rectangular, microscopic plates, and does not melt at 330° ; it sublimes in yellow needles, dissolves in concentrated sulphuric acid with a violet coloration, and turns red when treated with soda, owing to the formation of a sodium derivative.

The *phthalone* $C_{17}H_{10}N_2O_4$, obtained from 2'-methylbenzimidazole-2-carboxylic acid under like conditions, resembles the preceding compound, and dissolves in concentrated sulphuric acid with a wine-red coloration.

The *phthalone* $C_{16}H_{10}N_2O_2$, derived from 2-methylbenzimidazole, separates from glacial acetic acid in a yellow, flocculent condition, but is dirty green when dry; it melts at 223 — 225° with previous

softening, is more readily soluble than the 2'-phthalones, and dissolves in concentrated sulphuric acid with a dark yellow coloration.

2'-Methylbenzimidazole-2-carboxylic acid, $C_9H_8N_2O_2$, is formed, together with traces of the dicarboxylic acid and oxalic acid, when 2 : 2'-dimethylbenzimidazole is warmed with potassium permanganate; it crystallises in colourless needles, melts at 305° with decomposition when quickly heated, and is almost insoluble in all ordinary solvents except glacial acetic acid and boiling water. It has only feeble acid properties, measurements of its electrical conductivity showing it to be 60 times weaker than benzoic acid and 5 times weaker than pyridineortho-carboxylic acid; its alkali salts are decomposed by acetic acid, its barium salt by carbonic acid. The *silver* salt, $C_9H_7N_2 \cdot COOAg$, is a colourless, voluminous compound, soluble in ammonia. The *copper* salt is crystalline and insoluble in water, but the *barium* salt and the alkali salts are readily soluble. The *nitrate*, $C_9H_8N_2O_2 \cdot HNO_3$, crystallises in small, lustrous needles, decomposes at $220-230^\circ$, and is sparingly soluble in cold water. The *hydrochloride*, $C_9H_8N_2O_2 \cdot HCl$, crystallises in needles melting at $317-318^\circ$; the *platinochloride* forms lustrous, orange prisms which contain $2H_2O$, the anhydrous salt being hygroscopic. When the acid is heated with soda-lime, it is converted into 2'-methylbenzimidazole.

Benzimidazole-2-carboxylic acid, $C_8H_6N_2O_2$, prepared by oxidising 2-methylbenzimidazole, crystallises in microscopic prisms, does not melt at 320° , and is insoluble or nearly so in all ordinary solvents except glacial acetic acid and alcohol. The *platinochloride* forms yellow, prismatic crystals, and, like the *nitrate*, is only sparingly soluble in cold water. The *copper* and *lead* salts are crystalline, but the *silver* salt is amorphous.

2-Methylbenzimidazole-2'-carboxylic acid, $C_9H_8N_2O_2 + \frac{1}{2}H_2O$, can be obtained by oxidising the benzylidene derivative of dimethylbenzimidazole (see above) with potassium permanganate; it crystallises in colourless, lustrous needles, and when heated very quickly, melts at 157.5° with evolution of carbonic anhydride. It has feeble basic properties and dissolves in mineral acids, but is reprecipitated on adding sodium acetate; its acid character, however, is strongly marked. The *silver* salt, $C_9H_7N_2O_2Ag$, is not appreciably soluble in boiling water; in aqueous solutions of the acid, ferrous sulphate produces a straw-yellow coloration. When the acid is distilled or boiled with glacial acetic acid, it is decomposed into carbonic anhydride and 2-methylbenzimidazole.

Benzimidazole-2 : 2'-dicarboxylic acid is produced when 2'-methylbenzimidazole-2-carboxylic acid is boiled with potassium permanganate, but oxidation takes place very slowly; the acid was isolated in the form of its *platinochloride*, $(C_9H_6N_2O_4)_2 \cdot H_2PtCl_6$, a reddish-yellow, crystalline compound sparingly soluble in cold water.

Nitrobenzimidazole, $NO_2 \cdot C_6H_3 < \begin{smallmatrix} NH \\ N \end{smallmatrix} > CH$, prepared by treating benzimidazole with a mixture of nitric and sulphuric acids below 30° , crystallises in microscopic needles, and melts at 203° ; it dissolves freely in acids, alkalis, and alkali carbonates. The *nitrate* crystallises in microscopic needles, and melts at about $210-215^\circ$ when slowly

heated. The reduction product of the nitro-compound is very unstable. F. S. K.

Opening the Benzimidazole Ring. By E. BAMBERGER and B. BERLÉ (*Annalen*, **273**, 342—363; compare *Abstr.*, 1892, 631, 632).—When benzimidazole is dissolved in dilute soda and benzoic chloride gradually added to the ice-cold solution, orthodibenzoylphenylenediamine separates in crystals and formic acid remains in solution; this decomposition takes place quantitatively. When orthodibenzoylphenylenediamine is heated at a temperature above its melting point, it is decomposed into 2'-phenylbenzimidazole, melting at 282° , and benzoic acid; the platinochloride of this imidazole contains 3 mols. H_2O when dried at 120° or over sulphuric acid.

2'-Methylbenzimidazole is decomposed by soda and benzoic chloride into orthodibenzoylphenylenediamine and acetic acid, whereas 2-methylbenzimidazole yields dibenzoyltoluylenediamine [$Me : NHBz_3$]₂ = 1 : 3 : 4].

Nitroorthodibenzoylphenylenediamine, $NO_2 \cdot C_6H_3(NHBz)_2$, prepared by treating nitrobenzimidazole (compare preceding abstract) with benzoic chloride and soda, crystallises in lustrous needles, melts at $235-236^{\circ}$, and gives an intense yellowish-red coloration with potash, owing to the formation of a salt, which, however, is decomposed by water.

α -Dibenzoyldiamidoethylene, $C_2H_4(NHBz)_2$, is formed, together with traces of the β -compound, when glyoxaline is treated with soda and benzoic chloride in the cold. It crystallises from boiling alcohol in transparent, colourless, monoclinic prisms, $a : b : c = 0.5215 : 1 : ?$, $\beta = 83^{\circ} 41'$, melts at $202-203^{\circ}$, and dissolves freely in most organic solvents, and in concentrated mineral acids. Molecular weight determinations by the boiling point method, chloroform being used, gave results agreeing well with the theoretical.

β -Dibenzoyldiamidoethylene, $C_2H_4(NHBz)_2$, is formed when the α -compound is heated with acetic acid. It crystallises from boiling alcohol in small, lustrous needles, decomposes at $280-290^{\circ}$, and is much more sparingly soluble in the ordinary organic solvents and in hydrochloric acid than the α -compound just described. Both compounds are rather quickly decomposed by boiling glacial acetic acid, yielding brown products, the nature of which has not yet been determined, but they are not decomposed by boiling alcoholic potash; their isomerism is probably stereochemical and comparable with that of maleic and fumaric acids.

3'-Benzoylbenzimidazole, $C_{14}H_{16}N_2O$, can be obtained by warming benzimidazole with benzoic chloride. It crystallises in slender needles or plates, melts at $91-92^{\circ}$, and is readily decomposed by boiling water and by cold mineral acids into benzimidazole and benzoic acid; when treated with 10 per cent. potash at the ordinary temperature, it does not yield formylbenzoylphenylenediamine, as might have been expected, but is converted into benzoic acid, benzimidazole, and a compound melting at $134-135^{\circ}$, the nature of which was not ascertained. F. S. K.

Addition of Chloral to Quinoline Bases and Benzimidazoles. By E. BAMBERGER and B. BERLÉ (*Annalen*, 273, 364—373).—Paratoluquinoline combines readily with chloral, forming a compound of the composition $C_{10}NH_9, C_2HCl_3O + H_2O$; this crystallises in transparent prisms, melts at 79° , previously softening, and is decomposed into its components when kept over sulphuric acid under reduced pressure or when boiled with water. Paratoluquinoline also combines with anhydrous zinc chloride, forming a crystalline compound which melts at 229° and has the composition $(C_{10}NH_9)_2, ZnCl_2$.

A compound of the composition C_9NH_7, C_2HCl_3O is formed when quinoline is mixed with chloral; it crystallises in lustrous prisms, and melts at 63 — 65° .

2 : 2'-Dimethylbenzimidazole combines with chloral even in the cold, yielding a colourless, crystalline substance of the composition $C_{11}H_9N_2Cl_3$, which contains $1\frac{1}{2}$ or $2H_2O$; it has no definite melting point, and is decomposed by boiling water.

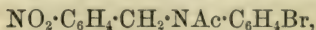
The compound obtained by the combination of benzimidazole and chloral is a colourless, granular substance, which melts at 122 — 131° with decomposition, and has the composition $C_7H_6N_2, C_2HCl_3O + H_2O$.

F. S. K.

Formula of Glyoxaline. By A. WOHL and W. MARCKWALD (*Ber.*, 26, 973—975).—The authors (Abstr., 1888, 624, 866) proved the correctness of Japp's formula long before Bamberger (Abstr., 1892, 632). They now defend the validity of their proof against his recent remarks (this vol., i, 432, *et seq.*).

C. F. B.

Formation of Dihydroquinazolines: a New Example of Intramolecular Transposition. By O. WIDMAN (*J. pr. Chem.* [2], 47, 343—366; compare Abstr., 1890, 1258).—*Orthonitrobenzylparabromaniline*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4Br$, is made by heating orthonitrobenzyl chloride (1 part) with parabromaniline (4 parts) for three-quarters of an hour on the water-bath. It crystallises in yellow, vitreous prisms or long, four-sided tables, and melts at 84 — 85° . Its crystallography is detailed. The *acetyl* derivative,



crystallises in white, rhombic, or six-sided tables, melts at 137 — 138° , and is nearly insoluble in ether and only sparingly soluble in hot alcohol.

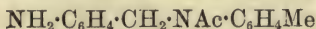
Orthamidobenzylacetanilide was described by Paal and Krecke (Abstr., 1892, 80) as being obtained when orthonitrobenzylacetanilide is reduced by tin and hydrochloric acid, but not when zinc and glacial acetic acid are used; they give its melting point as 126 — 127° . The author reduced the nitro-derivative with zinc and hydrochloric acid in alcohol, and with zinc and glacial acetic acid, and in both cases obtained a product which is undoubtedly orthamidobenzylacetanilide; it crystallises in small, colourless tables and in an ill-defined form, and melts at 80 — 81° . When heated with acetic anhydride, it yields orthacetamidobenzylacetanilide (m. p. 121° ;

Paal and Krecke, *loc. cit.*), whereas the methylphenyldihydroquinazoline (Paal and Krecke, Abstr., 1890, 1443) remains unchanged. When heated with hydrochloric acid, it is converted into *orthamidobenzylaniline dihydrochloride*, which crystallises in rectangular tables, melts at 183—185°, and dissolves easily in water.

Orthamidobenzylacetoparabromaniline is obtained by reducing the nitro-derivative (see above) with zinc in glacial acetic acid; it crystallises in colourless tables, and melts at 106—107°. Its crystallography is given.

The author concludes that the obtaining of Paal and Krecke's methylphenyldihydroquinazoline (*loc. cit.*) is not an accident of reduction.

The crystallography of *orthamidobenzylacetoparatoluidide*,



(Abstr., 1890, 1258), is given. When its solution in dilute hydrochloric acid is allowed to remain at the ordinary temperature for a week, it undergoes intramolecular transposition, and is converted into *orthacetamidobenzylparatoluidine*, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \text{Me}$; this crystallises in long needles, melts at 141°, and dissolves easily in hot alcohol and chloroform, but only sparingly in ether, light petroleum, or cold alcohol. Hydrolysis by hydrochloric acid converts it into *orthamidobenzylparatoluidine*. When treated with sodium nitrite and hydrochloric acid, it yields *acetamidobenzylnitrosoparatoluidine*, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}(\text{NO}) \cdot \text{C}_6\text{H}_4 \text{Me}$, which crystallises in pale yellow needles, and melts at 115—116°.

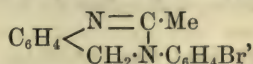
Orthacetamidobenzylaniline, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NHPh}$, is the product of a similar intramolecular transposition of *orthamidobenzylacetanilide* in hydrochloric acid. It crystallises in brittle prisms, melts at 125°, and is undoubtedly identical with the compound described by Paal and Krecke as *orthamidobenzylacetanilide* (Abstr., 1892, 80). The *hydrochloride* crystallises in tables or prisms, and melts at 180°; its solutions become green in air. The *chromate* crystallises in slender, yellow needles, very sparingly soluble in cold water. The *nitroso-derivative*, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NO}$, crystallises in colourless needles, and melts at 112—113°. The author is of opinion that the substance (m. p. 178°) obtained by Paal and Krecke (*loc. cit.*) by oxidising *orthacetamidobenzylaniline* by potassium permanganate is *orthacetamidobenzoic acid*.

Orthacetamidobenzylparabromaniline, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \text{Br}$, is the transposition product of *orthamidobenzylacetoparabromanilide*, and is similarly prepared; it crystallises in prisms, and melts at 148—149°.

When *orthamidobenzylacetanilide* is heated with dilute hydrochloric acid and alcohol in a reflux apparatus, the hydrochloride of 2-methyl-3-phenyldihydroquinazoline (with $2\text{H}_2\text{O}$) is obtained; this melts at 263°, and agrees in properties with the hydrochloride of the base obtained by Paal and Krecke (Abstr., 1890, 1443) by reducing orthonitrobenzylacetanilide with tin and hydrochloric acid. The free base crystallises in thin laminæ, and melts at 80°. The stannochloride forms white needles, and melts at 122—123°.

2-Methyl-3-paratolyldihydroquinazoline, $C_6H_4 < \begin{matrix} N=C \cdot Me \\ | \\ CH_2 \cdot N \cdot C_6H_4 \cdot Me \end{matrix}$, is obtained when orthamidobenzylacetoparatoluidide is heated with hydrochloric acid in a similar manner; it crystallises in white tables, and melts at 104—106°. The *stannochloride* crystallises in long, white needles, and melts at 139—140°.

2-Methyl-3-parabromophenyldihydroquinazoline,



is similarly prepared from orthamidobenzylacetobromanilide; it crystallises in long needles, and dissolves easily in alcohol; the *hydrochloride* is sparingly soluble.

When these three "anhydro-bases" are boiled with such solvents as benzene and light petroleum, they are decomposed; thus, in the case of the phenyl derivative, a white powder separates, which melts at 89° and dissolves in alcohol, the solution giving a precipitate with water which is yet a third substance, for it melts at 140°. So also the bromophenyl derivative yields a powder which melts at 110°, dissolves in glacial acetic acid, and, on dilution, yields crystals which melt at 168—169°.

The above researches show that Paal and Krecke failed to differentiate between the reduction products of orthonitrobenzylacetanilide and the transposition and condensation products of the action of hydrochloric acid on the amido-derivative obtained by the reduction (*loc. cit.*). Another correction has to be made in the statements of these authors; they obtained 2-methyl-3-phenyldihydroquinazoline by distilling orthamidobenzylacetanilide. Now it has been shown above that the compound which they thus named is, in reality, orthacetamidobenzylaniline, which undoubtedly would yield the quinazoline when distilled, for the present author has distilled orthacetamidobenzyltoluidine and obtained the corresponding quinazoline; he has, however, failed to obtain quinazolines by distilling orthamidobenzylacetanilide and orthamidobenzylacetoparatoluidide.

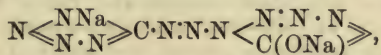
A. G. B.

Tetrazole Derivatives from Diazotetrazotic acid. By J. THIELE and J. T. MARAIS (*Annalen*, 273, 144—160; compare Abstr., 1892, 1295).—When a dilute (about 2 per cent.) solution of amidotetrazotic acid is diazotised with hydrochloric acid and sodium nitrite, the solution of diazotetrazole does not explode at ordinary temperatures, but decomposes quietly when boiled, with evolution of nitrogen and cyanogen; quantitative experiments showed that about 95 per cent. of the diazotetrazole is decomposed, in accordance with the equation $2CN_6 = C_2N_2 + 5N_2$, the remainder being probably converted into hydroxytetrazole and nitrogen, $CN_6 + H_2O = CH_2N_4O + N_2$. Assuming that diazotetrazole, like the diazobenzenesulphonic acids, exists in solution as an inner anhydride, its constitution may

be expressed by the formula $N < \begin{matrix} N:C-N \\ | \\ N \cdot N-N \end{matrix}$.

Sodium diazotetrazotate, $N \begin{smallmatrix} \text{N} \cdot \text{N} \\ \text{N} \cdot \text{Na} \end{smallmatrix} \rangle C \cdot N \cdot N \cdot ONa$, is formed when an aqueous solution of diazotetrazotic acid is neutralised with soda; as the salt is extremely soluble in water but insoluble in all other liquids, very special precautions have to be taken in order to obtain it in a pure condition. It is precipitated from its aqueous solution in colourless needles on the addition of alcohol; its solution has a strongly alkaline reaction, and only slowly undergoes decomposition when boiled, provided that carbonic anhydride be excluded. The dry salt decomposes suddenly, but not explosively, when heated, and is decomposed by concentrated sulphuric acid with production of flame. The *barium* salt was obtained, in an impure condition, as a yellow powder, readily soluble in water with alkaline reaction; its aqueous solution gives a precipitate of tetrazoleazo- β -naphthylamine (*loc. cit.*) on treatment with β -naphthylamine and acetic acid.

A *sodium* compound of the composition $C_2N_{10}ONa_2 + 5H_2O$ is obtained in yellow plates when a moderately concentrated solution of sodium diazotetrazotate is boiled for a long time and then cooled; apparently the same compound is formed when carbonic anhydride is passed into a boiling solution of the diazo-salt, but in both cases the yield is small. The dry substance explodes with great violence when heated at about 170° , and its aqueous solution gradually undergoes decomposition on boiling, with evolution of gas; in its aqueous solution, many metallic salts produce crystalline or amorphous precipitates, but β -naphthylamine gives no reaction. The constitution of the compound is possibly represented by the formula



that is to say, it is possibly a sodium derivative of hydroxyazotetrazole; the fact that, though highly coloured, it is converted into a colourless substance on treatment with reducing agents supports this view. The corresponding *barium* derivative, $C_2N_{10}O\text{Ba} + 4H_2O$, is comparatively sparingly soluble in water, from which it crystallises in small, yellow needles; it is highly explosive.

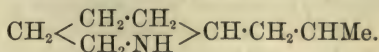
Benzaltetrazylyhydrazine, $CN_4H \cdot NH \cdot N \cdot CHPh$, is formed when a dilute solution of diazotetrazole is poured into a well-cooled mixture of stannous chloride and concentrated hydrochloric acid, and the solution then treated with benzaldehyde. It crystallises in lustrous needles, melts at 235° , and has moderately strong acid properties, dissolving freely in ammonia and alkali carbonates. The *sodium* derivative, $C_8H_7N_6Na + 3H_2O$, crystallises in prisms, and is readily soluble in water. The *calcium* derivative, $(C_8H_7N_6)_2Ca$, and the *barium* derivative crystallise with $6H_2O$, and effloresce on exposure to the air.

Tetrazylyhydrazine, $N \begin{smallmatrix} \text{N} \cdot \text{N} \\ \text{NH} \end{smallmatrix} \rangle C \cdot NH \cdot NH_2$, can be prepared by boiling the benzal derivative with 25 per cent. hydrochloric acid, and then decomposing the hydrochloride which is formed with sodium acetate in an atmosphere of carbonic anhydride. It forms yellowish, crystalline aggregates, melts at 199° with decomposition, and is in-

soluble in alcohol and ether; it is very readily oxidised, its aqueous solution turning red on exposure to the air or on the addition of a trace of ferric chloride. It has a strongly acid reaction, dissolves readily in alkalis and ammonia, and forms a colourless, insoluble silver derivative and a green copper derivative; it also forms moderately stable salts with acids. The *hydrochloride*, $\text{CN}_6\text{H}_4\cdot 2\text{HCl}$, crystallises in colourless needles, and melts at 176° ; its aqueous solution undergoes partial dissociation on evaporation at 100° .

Methyltetrazylpyrazolone, $\begin{array}{c} \text{CH}-\text{CO} \\ || \\ \text{CMe}\cdot\text{NH} \end{array} > \text{N}\cdot\text{C} < \begin{array}{c} \text{N}-\text{N} \\ || \\ \text{NH}\cdot\text{N} \end{array}$, is produced when tetrazylhydrazine is boiled with excess of ethylic acetoacetate. It crystallises from hot water in colourless needles, and melts at 215° with decomposition; it has an acid reaction, gives an intense yellow coloration with sodium nitrate, and with ferric chloride a brownish-violet coloration which becomes violet on diluting largely, brownish-yellow on adding acids. F. S. K.

A Homologue of Coniïne. By F. JACOBI and C. STOEHR (*Ber.*, 26, 949—951).—When α -isobutylene-pyridine (Abstr., 1891, 81) is reduced with sodium ethoxide, it yields a *methylconiïne*,



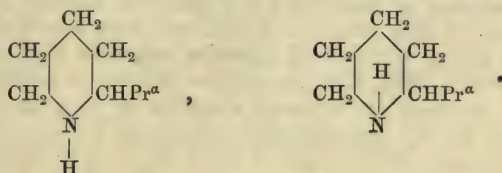
The pure base is a colourless liquid of sp. gr. $0^\circ/4^\circ = 0.8583$. It has the same odour and solubility as coniïne, boils at 181 — 182° (mercurial thread entirely in the vapour), and is volatile with steam. The *hydrochloride* forms colourless needles, and melts at 194 — 195° ; the *platinochloride* melts at 186 — 187° with decomposition; the *hydriodide* crystallises in long needles or prisms, and melts at 208 — 209° ; whilst the *cadmioidide* crystallises in monosymmetric prisms, and melts at 131 — 132° . A. R. L.

Isoconiïne and the Asymmetrical Nitrogen Atom. By A. LADENBURG (*Ber.*, 26, 854—865).—When dry coniïne hydrochloride is distilled with one-fourth its weight of zinc-dust, it yields, in addition to conyrine and unaltered coniïne, a quantity of a new base isomeric with the latter, for which the author proposes the name *isoconiïne*. It is separated from coniïne by treating the mixed platinochlorides with alcohol and ether, which dissolves the coniïne platinochloride, leaving the isoconiïne salt as a residue, from which the free base may be obtained in the usual manner. In most of its properties, isoconiïne closely resembles coniïne; it has almost the same boiling point and specific gravity, and its hydrochloride melts at the same temperature. The platinochlorides, however, differ considerably, that of isoconiïne being, as already stated, insoluble in alcoholic ether; it is dimorphous, crystallising in rhombic prisms, $a:b:c = 0.6955:1:0.3818$, melting at 172 — 175° , and in monosymmetric crystals melting at 160° . It rotates the plane of polarised light to the right, but to a less extent than coniïne, $[\alpha]_D$ being 8.19 and 13.79 in the two cases. It might therefore be supposed that isoconiïne is a mixture of dextro- and inactive coniïne, but this view cannot be correct, as the base, even

when prepared in a varying manner, has always the same rotatory power. Moreover, it is not formed by distilling inactive coniine with zinc-dust, and the specific rotatory powers of benzoylconiine and benzoylisoconiine, although different, do not stand to one another in the same ratio as those of the free bases, which would be the case if the substance were a mixture of dextro- and inactive coniine.

In order to ascertain whether the isomeride was formed from coniine by the conversion of the propyl into the isopropyl group, it was distilled with an excess of zinc-dust; the product was, however, found to be identical with the base obtained in a similar manner from coniine. Hence isoconiine also contains the propyl group, and is structurally identical with coniine, the two compounds being, therefore, stereometrical isomerides.

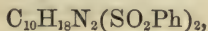
To account for the existence of such isomerides in piperidine derivatives, the author propounds a hypothesis according to which the valencies of nitrogen atom in piperidine and compounds containing similar nuclei do not all lie in the same plane, and suggests that the isomerism now under consideration is caused by the position of this valency relatively to the other groups in the molecule. Thus, in the present case two isomerides would be possible, according as the third valency of the nitrogen atom is on the same side or on the opposite side to the propyl group. It is also possible to explain the existence of the two isomerides if the valencies of the nitrogen atom all lie in the same plane, the third valency being in the one case inside, and in the other outside, the ring, as shown in the following formulæ.



Further investigations are in progress to ascertain if similar isomerides can be prepared from other piperidine derivatives. Results have been obtained in the case of dextro- α -pipecoline which appear to be analogous to those obtained with dextro-coniine.

H. G. C.

Nicotine. By A. PINNER (*Ber.*, **26**, 765—771).—The author replies to a recent paper by Blau (this vol., i, 375). By the interaction of nitrosohexahydronicotine, $\text{C}_{10}\text{H}_{18}\text{N}_2(\text{NO})_2 + \frac{1}{2}\text{H}_2\text{O}$, and phenylsulphonic chloride, *phenylsulphonehexahydronicotine*,



is formed. It crystallises from alcohol, melts at $133\text{--}134^\circ$, and is insoluble in alkali, thus proving that hexahydronicotine contains two imido-groups. Hexahydronicotine, which was the sole product obtained by the reduction of nicotine with sodium amalgam, yields two bromo-additive products; these are being further investigated, the one, $\text{C}_{10}\text{H}_{20}\text{N}_2 \cdot 2\text{HBr}_3$, is red and unstable, the second, $\text{C}_{10}\text{H}_{20}\text{N}_2 \cdot \text{HBr} \cdot \text{HBr}_3$, is yellow.

The author has already described the action of hydrochloric acid on dibromocotinine (this vol., i, 286). After treating the product with mercuric chloride and removing the mercury, two compounds can be precipitated by potassium carbonate; the more sparingly soluble substance, which it is proposed to term *apocotinine*, $C_9H_9NO_3$, crystallises from water in yellow plates, melts at 160° , and forms salts with acids and bases. The *copper salt*, $(C_9H_9NO_3)_2Cu + H_2O$, is crystalline. The second compound precipitated by potassium carbonate is *bromocotinine*, $C_9H_{11}BrN_2O$; it crystallises from water in long, colourless needles, melts at 120° , and undergoes decomposition at higher temperatures. Most of the salts of this base are readily soluble.

Cotinine, $C_{10}H_{12}N_2O$, is easily reduced by means of sodium in alcoholic solution, ammonia being eliminated; the remaining reduction products are being investigated.

J. B. T.

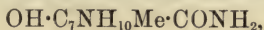
Decomposition of Salts of Nicotine and the Action of Alcohol on them. By R. NASINI and A. PEZZOLATO (*Gazzetta*, 23, i, 43—58; compare Abstr., 1891, 771).—The electrical conductivity of nicotine in aqueous solution is less than that of ammonia, and increases with dilution just as in the case of that base; that nicotine is a feeble base is also shown by the fact that dilute aqueous solutions, containing the alkaloid and hydrochloric or acetic acid in molecular proportion, exhibit a contraction on mixing, instead of the augmentation of volume noticed with strong bases and acids. Even when pure nicotine and pure liquid acetic acid are mixed in molecular proportion, a contraction of about 2.5 per cent. in volume occurs. The rotatory power of this mixture of the base with acetic acid at 20° is $[\alpha]_D = -72.21^\circ$, a number of opposite sense to that assigned by Schwebel (Abstr., 1883, 354) to nicotine acetate in aqueous solution. The specific rotation in aqueous solution is $[\alpha]_D = +49.68^\circ$; on adding water to the levorotatory anhydrous acetate, the rotation gradually decreases until, when 5 mols. H_2O have been added for every molecule of the salt, the solution becomes dextrorotatory; Schwebel's formula for the rotation, however, holds fairly well even for a solution containing 65 per cent. of the acetate. Alcoholic solutions of the salt are always levorotatory, $[\alpha]_D = -59^\circ$ to -65° , and on adding alcohol to dilute aqueous solutions the dextro-rotation is lessened. The addition of the corresponding quantity of triethylamine to an alcoholic solution of nicotine acetate completely decomposes the salt, for the specific rotation of the nicotine present then assumes the same value as that of nicotine itself in alcoholic solution. Complete decomposition of the salt does not occur on adding aniline or ammonia; boric acid slightly lowers the specific rotation of nicotine in alcoholic solution.

Much the same behaviour is noticed with the sulphate and hydrochloride as with the acetate; aqueous solutions of these salts are dextrorotatory, whilst alcoholic solutions are strongly levorotatory. Polarimetric measurements made on the acetate in benzene solution show that the levo-rotation is about the same as in alcoholic solutions; cryoscopic determinations in benzene solution give a molecular depression indicating the existence of the salt as such.

The authors conclude that nicotine has much more pronounced basic properties in aqueous solutions than in alcoholic; this is confirmed by the observation that the salts of this alkaloid are more readily decomposed by stronger bases in alcoholic than in aqueous solutions. The fact that nicotine and similar alkaloids (compare Menschutkin, Abstr., 1883, 708) are more strongly basic in aqueous solution is satisfactorily explained by assuming the formation of hydrates; on the addition of acids to such aqueous solutions, salts of the more active hydrated base are formed, whilst the slight stability of the salts, when dissolved in other solvents, is due to their being compounds of the more feeble anhydrous base.

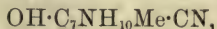
W. J. P.

Amides of Ecgonine. By A. EINHORN and F. K. DE NORWALL (*Ber.*, 26, 962—973; compare this vol., i, 378).—Aqueous ammonia merely hydrolyses the methylic salt of ecgonine. Alcoholic ammonia, however, at 100°, converts the *l*-salts into *l*-ecgonineamide,



which melts at 198°, and forms lustrous, rhombic prisms or needles, $a : b : c = 0.7199 : 1 : 0.5459$. Curiously enough, the *r*-methylic salt is by this treatment converted into the ethylic salt; with methylalcoholic ammonia, however, at 150°, it yields *r*-ecgonineamide, which melts at 173°, and forms large crystals, or a felted mass of small needles. The following salts were prepared:—Of *l*-ecgonineamide: the *hydrochloride*, $\text{C}_9\text{H}_{16}\text{N}_2\text{O}_2\cdot\text{HCl}$, white needles melting with decomposition at 275°; the *aurochloride*, $\text{C}_9\text{H}_{16}\text{N}_2\text{O}_2\cdot\text{AuCl}_4 + 1\frac{1}{2}\text{H}_2\text{O}$, yellowish needles melting at 70—80°, when anhydrous at 140—142°; the *platinochloride*, $(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_2)_2\cdot\text{H}_2\text{PtCl}_6$, orange plates melting with decomposition at 239°; the *hydrobromide*, with H_2O , large prisms melting with decomposition at about 260°; the *hydriodide*, with H_2O , monoclinic plates, or staurolitic twins, melting at 245°; the *picrate*, with H_2O , needles melting at 150°. Of *r*-ecgonineamide: the *hydrochloride*, large prisms melting at 268°; the *picrate*, needles melting at 177°. Both amides, when heated at 95° with alcoholic methylic iodide, yield *methiodides*, $\text{C}_{10}\text{H}_{19}\text{N}_2\text{O}_2\cdot\text{I}$; the *l*-variety forms tables or needles melting at 203°, the *r*-variety, with H_2O , plates melting at 220°; along with the former a second iodo-compound, melting at 223°, was obtained.

Benzoic chloride by itself has no action on ecgonineamide when the two are taken in molecular proportion. If excess of benzoic chloride is used at 100°, the *l*-amide yields *l*-ecgoninenitrile,



as needles melting at 145.5°; *hydrochloride*, $\text{C}_9\text{H}_{16}\text{N}_2\text{O}\cdot\text{HCl}$, forms small lustrous plates. The *r*-amide under these conditions yields *benzoyl-r*-ecgoninenitrile, $\text{OBz}\cdot\text{C}_7\text{NH}_{10}\text{Me}\cdot\text{CN}$, as very soluble crystals; the *hydrobromide*, $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2\cdot\text{HBr}$, needles melting at 210°; the *platinochloride*, $(\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2)_2\cdot\text{H}_2\text{PtCl}_6$, flesh-coloured needles; the *picrate*, needles melting at 227°. The corresponding *benzoyl-l*-ecgoninenitrile was obtained from the *l*-nitrile with benzoic chloride in ethylic acetate solution, and also directly from the *l*-amide by the action of benzoic

at 105° ; in the presence of soda; it forms fern-like crystals melting. chloride the *hydrochloride*, + HCl, white plates or lustrous prisms. *Acetyl-r-ecgonine*, $\text{OAc}\cdot\text{C}_7\text{NH}_{10}\cdot\text{CN}$, was obtained as an oil by boiling the *r*-amide with acetic anhydride; its *hydriodide*, $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_2\cdot\text{HI}$, forms white needles with satiny lustre melting with decomposition at 243° .

C. F. B.

Hygrineoxime. By C. LIEBERMANN and O. KÜHLING (*Ber.*, 26, 851—852).—This substance, $\text{C}_5\text{H}_{15}\text{N}\cdot\text{NOH}$, obtained from "low-boiling hygrine," $\text{C}_5\text{H}_{15}\text{NO}$, and hydroxylamine, forms white crystals melting at 116 — 120° ; its formation shows that the oxygen in hygrine must be in the carbonyl condition. It forms no definite compound with platinum, gold, or mercuric chlorides, or with potassium mercuriodide, but it yields a *picrate*, $\text{C}_8\text{H}_{16}\text{N}_2\text{O}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, as needles melting at 160° , and, when boiled with methyl alcohol and methylic iodide, yields *methyhygrineoxime hydriodide*, $\text{C}_8\text{H}_{15}\text{MeN}_2\text{O}\cdot\text{HI}$, as white needles.

C. F. B.

Alkaloids of *Corydalis nobilis*. By E. BIRSMANN (*Chem. Centr.*, 1893, i, 35; from *Inaug. Diss.*, Dorpat, 1892).—The plant and root were extracted with dilute alcohol, the alcohol evaporated, the residue acidified and washed with light petroleum. The liquid is then extracted with benzene (1), the aqueous solution supersaturated with sodium carbonate, when a brown resin (2) separates, and the alkaline solution extracted with chloroform (3). The benzene extract (1) is treated with a little strong alcohol to precipitate tannin, then treated with very dilute hydrochloric acid, and the acid extract precipitated with soda. After recrystallisation, an alkaloid, $\text{C}_{21}\text{H}_{21}\text{NO}_4$, is obtained, which melts at 128° , has $[\alpha]_D = +276.6^{\circ}$, and is soluble in chloroform and benzene. From the resin (2), by purification with alcohol and crystallisation from much water, *corydalinobiline*, $\text{C}_{22}\text{H}_{25}\text{NO}_3$, is obtained; this is probably identical with Wackenroder's corydaline. It yields well characterised salts, including an aurochloride and platinochloride. From the chloroform solution (3), four bases were isolated, but were not investigated further.

A. J. G.

Geissospermine. By M. FREUND and C. FAUVET (*Ber.*, 26, 1084—1085).—Hesse (*Abstr.*, 1880, 675) obtained from pereiro bark (*Geissospermum Vellozii*) a crystalline alkaloid, geissospermine, and an amorphous alkaloid, pereirine, melting at 124° .

The authors have examined a crystalline alkaloid which has for some time been placed on the market by the firm of Trommsdorf under the name of geissospermine. Analyses of the base and of its salts show that it has the formula $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}_4$; its salts contain but one equivalent of acid, and in this respect as well as in its physiological action it resembles brucine. It melts at 189° , and is readily converted into an amorphous base $\text{C}_{46}\text{H}_{54}\text{N}_4\text{O}_7$, which is tetracidic, melts at 60 — 70° , yields a *methiodide* melting at 265° , and, when fused with potash, gives rise to a crystalline base melting at 151° .

A. R. L.

Stachydrine. By A. v. PLANTA and E. SCHULZE (*Ber.*, **26**, 939--942).—*Stachydrine* is the name adopted by the authors for the base resembling betaine, from *Stachys tuberifera* (*Abstr.*, 1890, 1183). They describe methods for its isolation. The *hydrochloride*, $C_7H_{13}NO_2.HCl$, crystallises in transparent prisms, is readily soluble in water, and differs from betaine hydrochloride both in composition and in being soluble in cold absolute alcohol. The *platinochloride*, $(C_7H_{13}NO_2)_2.H_2PtCl_6$, forms large, orange-red, rhombic crystals containing $2H_2O$, $a:b:c = 0.6082:1:0.8277$; the *aurochloride* crystallises in small, yellow prisms. The free base, obtained by treating the hydrochloride with silver oxide, forms colourless, transparent crystals which deliquesce in the air, and become opaque with the loss of water of crystallisation at 100° ; it melts at 210° , and its aqueous solution has not an alkaline reaction. A. R. L.

Amyloid, a Component of Milk and Dairy Products. By F. J. HERZ (*Chem. Zeit.*, **16**, 1594—1595).—During the microscopic investigation of milk, cream, curds, butter-fat, and lean cheese, and even of pure casein, the author has found structures which, as regards shape and size, are not unlike starch granules, and which also give a bluish colour with iodine. They are, however, not gelatinised on boiling with water, and are also insoluble in hot alcohol and ether.

The author thinks that they consist of a modification of albumin, and may perhaps be obtained in a pure state by treating milk or colostrum with pepsin and hydrochloric acid. L. DE K.

Oxyhæmatin, reduced Hæmatin, and Hæmochromogen. By H. BERTIN-SANS and J. MOITESSIER (*Compt. rend.*, **116**, 401—403).—Oxyhæmatin, prepared by Cazeneuve's process and dissolved in a 1 per cent., or 0.1 per cent., solution of sodium hydroxide, shows a single absorption band between C and D, the middle being about $\lambda 618$. The addition of a reducing agent, such as potassium sulphide, sodium hydrosulphide, ferrous tartrate, &c., produces the true spectrum of reduced hæmatin, a single absorption band, the middle of which practically coincides with D. This spectrum is not affected by the presence of an excess of the reducing agent. Reduced hæmatin, showing precisely the same spectrum, is obtained when the hæmatin has been dissolved in an alcoholic solution of sodium hydroxide or an aqueous solution of sodium carbonate.

If the solution of reduced hæmatin obtained in this way is mixed with a slight excess of ammonia, or of various amines, such as ethylamine, aniline, glycocine, or taurine, the absorption band of reduced hæmatin rapidly disappears, and the spectrum of hæmochromogen becomes visible.

Carbamide and other amides do not produce this result.

A very minute quantity of albumin, on the other hand, converts the spectrum of reduced hæmatin into that of hæmochromogen. 0.05 milligram of albumin is sufficient to produce this change in 2 c.c. of the solution of reduced hæmatin, and hence it constitutes a very delicate test for albumin.

Hæmochromogen solution, when treated with a current of air, is reconverted into oxyhæmatin. The position of the two bands of hæmochromogen varies with the nature of the nitrogen compound added to the hæmatin, but the middle of the first band, which is the more intense and better defined, oscillates about λ 560.

It follows, from these results, that when oxyhæmatin in alkaline solution is treated with reducing agents in absence of ammonia and other nitrogen compounds, it yields *reduced hæmatin*, which has a characteristic spectrum, whilst in presence of ammonia, amines, albumin, &c., hæmochromogen is formed. The differences in the spectrum of hæmochromogen are not due to the differences in the composition of the solvent, and it would seem that several hæmochromogens exist.

C. H. B.

Action of Carbonic Oxide on Reduced Hæmatin and Hæmochromogen. By H. BERTIN-SANS and J. MOITESSIER (*Compt. rend.*, 116, 591—592).—When carbonic oxide is passed into an alkaline solution of freshly prepared reduced hæmatin (preceding abstract), the single absorption band is replaced by two bands similar to those of carbonylhæmoglobin. The carbonic oxide, however, is very easily displaced by oxygen or air. Out of contact with air, the carbonic oxide is displaced by hydrogen, but the change takes place much more slowly.

If excess of ammonia is added to the solutions of carbonylhæmatin, the appearance of the spectrum changes immediately, and the two bands (which correspond approximately to λ 569 and λ 531) are replaced by two more distinct and intense bands at λ 590 and λ 546, the first being the narrower, more intense, and better defined of the two. The same phenomena are obtained by the direct action of carbonic oxide on the hæmochromogen obtained by the action of a reducing agent on ammoniacal solutions of oxyhæmatin (compare Popoff, *Centr. f. d. Med. Wiss.*, 1868). The ammonia not only alters the spectrum, but also increases the stability of the compound, the carbonic oxide being displaced much more slowly by oxygen.

If an excess of albumin is added to the solution of carbonylhæmatin, the appearance of the spectrum does not alter, but the compound becomes much more stable in presence of air, and addition of ammonia has no effect on the spectrum. The spectrum has exactly the same appearance as that of the compound formed by the action of carbonic oxide on hæmochromogen that has been prepared in presence of albumin. The instability of carbonylhæmatin, especially in the absence of albumin, and the effect of ammonia on its spectrum, distinguishes it readily from carbonylhæmoglobin.

C. H. B.

Organic Chemistry.

Preparation of Tetriodoethylene. By L. MAQUENNE (*Bull. Soc. Chim.* [3], 7, 777—778).—A simpler method of preparing tetriodoethylene, C_2I_4 , than that described by Moissan (*Abstr.*, 1892, 1291) consists in adding an excess of potash to an aqueous solution of acetylene, and subsequently dropping in iodine in small portions, when the tetriodoethylene separates as a crystalline precipitate. It is also obtained when crude barium carbide (*Abstr.*, 1892, 685; this vol., i, 62) is treated with an equal weight (30 grams) of iodine dissolved in benzene (75—100 c.c.); water is now added drop by drop until effervescence ceases, when the benzene solution is decanted from the pasty mixture of magnesia (from the crude barium carbide), the latter extracted with boiling benzene, and the united benzene solutions distilled and finally evaporated to dryness; the tetriodoethylene is then washed with alcohol and crystallised from hot benzene. The pure compound (6 grams) melts at 192° (corr.). The compound of lower melting point obtained by Homolka and Stolz (*Abstr.*, 1885, 1198) must have been impure. A. R. L.

Substitution in the Fatty Series. By A. D. HERZFELDER (*Ber.*, 26, 1257—1261).—Although propylenic bromide yields tribromhydrin when brominated, yet propylenic chloride does not yield trichlorhydrin, $CH_2Cl \cdot CHCl \cdot CH_2Cl$, boiling at 154 — 156° , when treated either with antimony pentachloride (1 mol.), or with liquid chlorine and iron. The trichloropropane actually formed, which is also formed when propylic chloride is treated with antimony pentachloride (2 mols.), boils at 132° , and differs also from that obtained by the action of antimony chloride on acetone chloride, which boils at 121° , and has the constitution $CH_3 \cdot CCl_2 \cdot CH_2Cl$. It must, therefore, have the only remaining formula $CH_3 \cdot CHCl \cdot CCl_2$, and the old boiling point—"about 140° "—formerly given for this substance is incorrect.

When propylic, isopropylic, butylic, isobutylic, and tertiary butylic chlorides, all containing either the group $>CCl \cdot CH_3$ or $>CH \cdot CH_2Cl$, are heated with bromine and iron wire, they all give dibromides containing the group $>CBr \cdot CH_2Br$. Isoamylic chloride, under similar circumstances, yields a monobromide, $CHMe_2 \cdot CH_2 \cdot CH_2Br$.

C. F. B.

Formation of Amylic Salts from Acids and Amylene. By W. NERNST and C. HOHMANN (*Zeit. physikal. Chem.*, 11, 352—390).—The formation of amylic salts from acids and amylenes (trimethylethylene) has already been investigated by Menshutkin and Konovaloff (*Abstr.*, 1888, 340 and 1167), the latter coming to the conclusion that the change is one which does not follow the ordinary law of mass action. This conclusion was, however, as shown by the authors, based upon an incorrect application of the above law, a recalculation of the numbers given by Konovaloff for the action of dichloroacetic acid on amylenes giving results in perfect accordance with those demanded

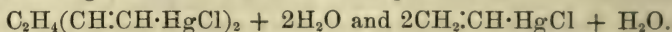
by theory. It therefore appeared desirable to submit the action of acids on amylene to a further examination, in order to ascertain whether the law of mass action holds throughout.

The acids taken were di- and tri-chloroacetic, trichlorobutyric, trichlorolactic, salicylic, and benzoic. Amylic trichloroacetate was prepared in the course of the experiments in a pure condition. It is a colourless liquid, of sp. gr. $20.4^{\circ}/4^{\circ} = 1.202$, and specific refraction $n_{20.4^{\circ}}/D = 1.44758$.

The formation of the ethereal salts takes place in all cases in accordance with the law of mass action. The limit to the action of an acid is defined by its affinity coefficient, this being carried further the greater the electrolytic dissociation in water of the acid in question. The action is also proportional to the square of the concentration of the acid.

H. C.

Action of Mercury Salts on Unsaturated Hydrocarbons and Alcohols. By M. G. KUTCHEROFF (*J. Russ. Chem. Soc.*, 24, 330—333).—With a solution of mercuric chloride, diallyl gives an abundant white precipitate, insoluble at the ordinary temperature in water or alcohol, but which dissolves easily in caustic alkalis, and may be reprecipitated from the solution by neutralisation. Acids, even acetic acid, dissolve it with liberation of diallyl. The empirical formula of the compound is $C_6H_{10}, HgCl_2, HgO, H_2O$. A similar substance having the composition $2C_2H_4, HgCl_2, HgO$ is precipitated when ethylene acts on an aqueous solution of mercuric chloride. It is slightly soluble in water and in alcohol, easily soluble in alkalis, and regenerates ethylene when treated with acids. The author attributes the following constitutions to these compounds:—



Allyl alcohol at the ordinary temperature gives a white, crystalline precipitate with aqueous mercuric chloride; this is soluble in alkalis, and has the composition $O(C_3H_4 \cdot HgCl)_2$. It may be considered as the compound of allyl ether corresponding with the above-mentioned compounds of diallyl and ethylene, and can, in fact, be formed directly from the ether and mercuric chloride. Allyl alcohol when heated for several hours at 100° with mercuric chloride is converted for the most part into allyl ether without any trace of allylic chloride being formed. Calomel and the compound $O(C_3H_4 \cdot HgCl)_2$ are the other products.

Negative results were obtained with commercial amylene.

J. W.

Synthesis of Erythritol. By G. GRINER (*Compt. rend.*, 116, 723—725).—When erythrene, $CH_2:CH:CH:CH_2$ is dissolved in a large quantity of chloroform, cooled at -21° and treated with bromine, it yields a liquid dibromide, $C_4H_6Br_2$, boiling at $74-76^{\circ}$ under a pressure of 26 mm. This compound is unstable in the liquid form, but at 100° it is very rapidly converted into a solid of the same composition, melting at $53-54^{\circ}$, and boiling at $92-93^{\circ}$ under a pressure of 15 mm. It is very volatile, sublimes easily, has a piquant odour, and is very irritating to the eyes.

When this dibromide is heated at $125-130^{\circ}$ for eight hours with

a slight excess of silver acetate and some acetic anhydride, it yields a diacetin, $C_4H_6(OAc)_2$, boiling at 110° under a pressure of 20 mm., and this combines readily with bromine forming the compound $C_4H_6Br_2(OAc)_2$ melting at 87° . The latter, when treated with silver acetate, yields a tetracetin, $C_4H_6(OAc)_4$, identical with that obtained from erythritol, and this tetracetin, when heated with concentrated barium hydroxide solution at 100° , yields erythritol, identical with the natural product in composition, melting point, crystalline form, and absence of optical activity.

C. H. B.

Trehalase, a Ferment for Trehalose. By E. BOURQUELOT (*Compt. rend.*, 116, 826—828).—The author's previous researches have shown that trehalose is almost always present in fungi, but only appears when the production of spores commences, and is localised in the tissues, and more especially in the vegetative tissue of the fruit or sporophore; it disappears gradually during ripening. Glucose cannot be detected in fungi until trehalose has made its appearance, but persists after the latter has disappeared. These facts indicated the presence of some ferment capable of converting trehalose into glucose, and the author has isolated such a ferment in the following manner.

Aspergillus niger is cultivated on Raulin's fluid, and when the liquid is covered with abundant fructifications, the growth is removed, its lower surface washed with water, triturated with dry sand, and left in contact with alcohol of 95° for five or six hours, after which it is collected and dried in a vacuum. It is then treated with water, again filtered, and the filtrate reprecipitated with alcohol, the precipitate being washed with alcohol and dried in a vacuum.

If a fermenting liquid only is required, it is sufficient to draw off the liquid when the mould is in full fructification and replace it by distilled water.

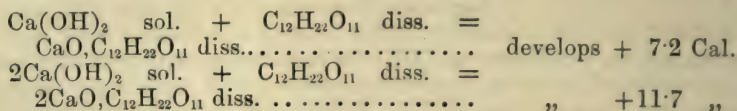
The ferment thus obtained completely converts trehalose into glucose, 1 mol. of the former yielding 2 mols. of the latter. Trehalose from the *tréhala* and trehalose from fungi both behave in precisely the same way under the influence of the ferment. Invertin from yeast, the diastase of the saliva, and emulsin have no action on trehalose. The author proposes to call the special ferment *trehalase*.

The product obtained also acts on maltose. It would seem, therefore, either that one and the same ferment acts on both trehalose and maltose, or that the product is a mixture of two ferments. Attempts to isolate two substances by fractional precipitation gave negative results. The power to ferment trehalose, however, diminishes above 54° , and completely disappears at about 63° , whereas the power to ferment maltose remains undiminished at 64° , and only disappears between 74° and 75° . It follows that the product obtained in the manner described is really a mixture of two substances, the one fermenting maltose, and the other fermenting trehalose.

C. H. B.

Calcium Sucrates. By P. PETIT (*Compt. rend.*, 116, 823—826).—The action of sodium hydroxide solution on a mixed solution of

saccharose and calcium chloride in a calorimeter gives the following results.



With a higher proportion of calcium oxide there is no further thermal disturbance, and hence it would seem that only two calcium sucates exist at the ordinary temperature. The action of monocalcium sucate on freshly precipitated calcium hydroxide leads to the same value, +4.5 Cal., for the formation of the dicalcium sucate. The following table shows the quantity of calcium oxide dissolved by 1 gram-molecule of sugar in various proportions of water.

Water.....	20	10	8	6	5	4 litres.
CaO	56.07	56.10	56.14	59.2	63.15	70.24 grams.
Water.....		3	2		1.5	litres.
CaO		78.88	88.06		93.23	grams.

The curve representing these results indicates that at infinite concentrations 2 mols. of calcium oxide would be dissolved.

Monocalcium sucate combines with saccharose, the heat developed by the addition of various proportions of saccharose to 1 mol. of the sucate being as follows.

1 mol.	2 mols.	3 mols.	5 mols.	7 mols.
+1.68	+2.8	+3.1	+2.9	+3.1 Cal.

It appears that beyond 3 mols. the thermal disturbance becomes constant, and hence there is one compound, $\text{CaO, C}_{12}\text{H}_{22}\text{O}_{11}, 3\text{C}_{12}\text{H}_{22}\text{O}_{11}$, formed with development of +3.1 Cal.

The author was unable to obtain a tricalcium sucate. When a sucate solution containing 19.2 per cent. of calcium oxide is heated at 100°, a dicalcium sucate is obtained, but it is only slightly soluble in water, and when treated with hydrochloric acid, the heat of formation obtained is +5.4 Cal. It follows that heat modifies the sucates very considerably, probably because calcium oxide acts on saccharose in much the same way as on maltose.

C. H. B.

Action of Metaphosphoric acid on Organic Bases. By W. SCHLÖMANN (*Ber.*, 26, 1020—1025).—The following bases in ethereal solution form amorphous metaphosphates on the addition of metaphosphoric acid (prepared by dissolving phosphoric anhydride in 4 parts of water): Methylamine, ethylamine, propylamine, amylamine, allylamine, ortho- and para-toluidine, xyloidine, α - and β -naphthylamine, benzylamine, anisidine, phenylhydrazine, unsymmetrical diphenylhydrazine, α -benzylphenylhydrazine, ethylenediamine, pentamethylenediamine, benzidine, ortho- and para-phenylenediamine, and toluenylenediamine. These salts are generally soluble in water or in excess of the acid, but insoluble in alcohol.

The metaphosphates of the following bases are readily soluble in ether, β -benzylphenylhydrazine, piperidine, methylaniline, diphenylamine, diamylamine, hydrazobenzene, pyridine, quinoline, and dimethylaniline.

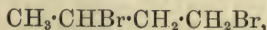
Solutions containing 3 per cent. of aniline and 0.1 per cent. of phenylhydrazine give precipitates with solutions of metaphosphoric acid containing 12.5 per cent. of phosphoric anhydride. On treating a mixture of aniline and methylaniline with metaphosphoric acid solution, the aniline is completely precipitated, but carries down some of the methylaniline salt.

β -Benzylphenylhydrazine, $\text{NHP} \cdot \text{NHC}_6\text{H}_5$, is prepared by heating phenylhydrazine with 2 molecular proportions of benzylic chloride for 24 hours at 160° ; it crystallises in pale yellow needles melting at 155.5° .
J. B. T.

Action of Nitrous acid on Tetramethylenediamine. By N. DEMYANOFF (*J. Russ. Chem. Soc.*, **24**, 346—355).—Tetramethylenediamine was prepared by reducing ethylenic dicyanide by means of sodium in methyl alcohol solution, and from its hydrochloride the nitrite was obtained by grinding it up with water and silver nitrite at the ordinary temperature. On heating an aqueous solution containing 50 grams of tetramethylenediamine nitrite in 1 litre of water, decomposition took place at 80 — 90° , and the heating was continued until a temperature of 130° was reached. Nitrogen was given off along with a gas which did not condense in the receiver, but was absorbed by bromine. The aqueous distillate was quite homogeneous, neutral, slightly yellow, and of an offensive odour.

The bromide formed by the union of the gaseous product of decomposition with bromine was a crystalline solid melting at 115 — 116° . Investigation showed it to be the tetrabromide of erythrene, $\text{CH}_2\text{:CH}\cdot\text{CH}\cdot\text{CH}_2$, which is consequently the hydrocarbon formed in the decomposition.

In the aqueous distillate, there were detected nitrosopyrrolidine, $\begin{matrix} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{matrix} > \text{N}\cdot\text{NO}$, tetrahydrofurfuran, $\begin{matrix} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{matrix} > \text{O}$, boiling at 67° , and an unsaturated alcohol of the formula $\text{C}_4\text{H}_7\cdot\text{OH}$. The latter boiled at 112 — 114° , and had a sp. gr. of 0.8635 at $0^\circ/0^\circ$, and 0.8484 at $18.5^\circ/0^\circ$. When heated with fuming hydrobromic acid, it gave a saturated dibromhydrocarbon, $\text{C}_4\text{H}_8\text{Br}_2$, boiling at 174 — 175° , and having a sp. gr. of 1.829 at $0^\circ/0^\circ$. The dibromhydrocarbon,



obtained from aldol by reduction and heating with fuming hydrobromic acid, was proved to be identical with the bromide from the unsaturated alcohol, which, therefore, must have the constitution $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ or $\text{CH}_2\text{:CH}\cdot\text{CHMe}\cdot\text{OH}$. The rate of etherification points to the first formula as being correct.

The brown residue which did not distil over at 130° consisted of two glycols, tetramethylene glycol, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, and the glycol $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$.
J. W.

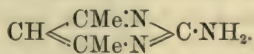
Action of Ammonia and of Aliphatic Amines on Acetylacetone. By A. COMBES and C. COMBES (*Bull. Soc. Chim.* [3], 7, 778—788).—*Acetylacetonamine*, $\text{CHAc}:\text{CMe}\cdot\text{NH}_2$, is formed with the elimination of water when the additive compound of ammonia and acetylacetone (*Bull. Soc. Chim.* [2], 49, 577) is gently heated in a current of ammonia and the product distilled; the compound passes over at 209° , solidifies in crystals on cooling, and melts at 43° . It undergoes hydrolysis when its aqueous solution is heated, and acids exert the same effect in the cold. The *hydrochloride* formed by passing dry hydrogen chloride into an ethereal solution of the compound dissociates on exposure; the copper derivative, $(\text{C}_6\text{H}_5\text{NO})_2\text{Cu}$, is crystalline. It reacts with methylic iodide, forming methylacetylacetone, and when it is heated at 220° for 15—18 hours, it blackens, and several basic compounds are formed, one of which has the formula $\text{C}_{15}\text{H}_{18}\text{N}_2$, and melts at 85° .

Acetylacetone reacts with ethylamine, forming a compound, $\text{CHAc}:\text{CMe}\cdot\text{NHEt}$, which boils at $210\text{--}215^\circ$, and with diethylamine, forming a compound, $\text{CHAc}:\text{CMe}\cdot\text{NEt}_2$, boiling at $155\text{--}156^\circ$ (24 mm.), but it does not act on tertiary amines. With ammonia, methylacetylacetone yields a compound, $\text{CMeAc}:\text{CMe}\cdot\text{NH}_2$, melting at 105° .

Dimethylacetylacetone, $\text{CMe}_2\text{Ac}:\text{CMe}$, prepared by the action of methylic iodide on the sodium derivative of methylacetylacetone, boils at $175\text{--}177^\circ$. It does not react with ammonia, a fact which indicates that acetylacetone and the other compounds react with ammonia in a tautomeric form, $\text{RCO}\cdot\text{CH}:\text{C}(\text{OH})\text{R}$, in which they contain a mobile (hydroxylic) hydrogen atom; it also justifies the adoption of the above formulæ for the amido-compounds.

Secondary amines containing an aromatic radicle do not react with acetylacetone. A. R. L.

Action of Diamines on Acetylacetone. By A. COMBES and C. COMBES (*Bull. Soc. Chim.* [3], 7, 788—793).—The compound formed by the action of ethylenediamine on acetylacetone has already been described (*Abstr.*, 1889, 851). The compound $\text{C}_7\text{H}_{12}\text{N}_4\text{O}_2$, obtained by the action of carbamide on acetylacetone (*Evans*, this vol., i, 129) melts at 200° with decomposition. Acetylacetone reacts with guanidine carbonate, forming an *amidodimethylpyrimidine*,



It separates from hot concentrated aqueous solutions in an anhydrous condition, and melts at 153° , but, on allowing a saturated solution to slowly cool, crystals containing $2\frac{1}{2}\text{H}_2\text{O}$ are obtained.

A. R. L.

Tar from the Bark of *Populus tremula*. By N. FARMAKOVSKY (*J. Russ. Chem. Soc.*, 24, 423—439).—The tar obtained from the dry distillation of *Populus tremula* is strongly acid, 1000 grams requiring 30 grams of anhydrous potassium carbonate for its neutralisation. The acid constituents are the lower fatty acids up to valeric acid, phenols (about 17 per cent.), and benzoic acid (about $\frac{1}{2}$ per cent.).

Hydrocarbons form the remainder of the tar. Its sp. gr. at 17°/17° is 0.956. J. W.

Condensation of Aliphatic Aldehydes with Cyanacetic acid. By E. FIQUET (*Bull. Soc. Chim.* [3], 7, 767—771).—The condensation of aliphatic aldehydes with cyanacetic acid is quite analogous to that of aromatic aldehydes (*Abstr.*, 1892, 1340). *Cyanocrotonic acid*, $\text{CHMe}:\text{C}(\text{CN})\cdot\text{COOH}$, is obtained by heating cyanacetic acid with an excess of acetaldehyde at about 93—95°. Care must be taken, as the acid decomposes at about 95°, and other condensations take place when the heating is protracted. The new acid crystallises in delicate, colourless needles, melts at 92°, is very soluble in water, and forms crystalline alkali salts. It yields malonic acid and ammonia when heated with potash, and oxalic acid when heated with nitric acid; when distilled, crotononitrile passes over at 120°. Trichlorocyanocrotonic acid is formed by heating a mixture of cyanacetic acid, chloral, and glacial acetic acid in a reflux apparatus for 48 hours.

Hexylcyanacrylic acid, $\text{CH}_2\text{Me}[\text{CH}_2]_4\text{CH}:\text{C}(\text{CN})\cdot\text{COOH}$, is prepared by boiling together a mixture of cenanthaldehyde, cyanacetic acid, and glacial acetic acid for 60 hours; it crystallises in nacreous laminæ, and melts at 116—118°.

Cyanacetic acid and glyoxylic acid react at 180°, forming a crystalline product melting at 210°; it may be either *cyanofumaric* or *cyanomalonic acid*. A. R. L.

Brom-additive Products of Angelic and Tiglic acids. By J. WISLICENUS (*Annalen*, 274, 99—119).—A rejoinder to Fittig (this vol., i, 188). The author brings forward fresh experimental evidence in support of his views (*ibid.*, i, 135). A. R. L.

Turkey-red Oil. By P. JUILLARD (*Chem. Centr.*, 1893, i, 185—187; from *Bull. Soc. indust. Mulhouse*, 1892, 415—491).—The products of the action of sulphuric acid on castor and olive oil, which are employed as substitutes for the original Turkey-red oil, have been the subject of numerous investigations; see Frémy (*Annalen*, 65, 121), Liechti and Suida (*Abstr.*, 1884, 238), Benedict and Ulzer (*Abstr.*, 1887, 914), and others.

The author finds that the initial product of the action of sulphuric acid on ricinoleic acid is ricinosulphuric acid, which reacts with another molecule of ricinoleic acid to form diricinosulphuric acid, which then hydrolyses in part into diricinic acid. Sulphuric acid can react with the latter, so that the red oil obtained in this manner consists of a mixture of mono- and poly-ricinic acids, and of mono- and poly-ricinosulphuric acids. With sulphuric acid, castor oil gives first ricinoleinsulphuric acid and a diricinoleinsulphuric acid, $\text{OH}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{COO}\cdot\text{C}_3\text{H}_5(\text{OH})\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{32}\text{O}\cdot\text{SO}_2\cdot\text{OH}$, which is soluble in water. Polyricinic acids and polyricinosulphuric acids are also formed. Diricinosulphuric acid decomposes on hydrolysis with boiling alcoholic potash, in a manner typical of the polyricinosulphuric acids, into ricinic acid and ricinosulphuric acid, but with dilute acids into sulphuric acid and diricinic acid. Diricinoleinsulphuric acid is converted by

alkali hydroxides and carbonates into ricinosulphuric acid, ricinic acid, and glycerol; whilst, when heated at 90° with a little dilute hydrochloric acid, sulphuric acid, glycerol, and polyricinosulphuric acid are the products. It is usual to wash the crude product with a concentrated solution of sodium sulphate to free it from acid; the author shows that the ricino- and ricinolein-sulphuric acids are thereby converted into their acid or normal salts according as they contain a single carboxyl group or otherwise.

For the estimation of the molecular weights of these acids by the cryoscopic method, the author employs phenol as solvent, taking the molecular depression of this compound to be 67.5. Eykman's value (76) is only correct with phenol for the ethereal salts of some bibasic acids. *Ricinic acid* is a syrup; the semi-fluid mass obtained by the decomposition of ricinosulphuric acid contains a compound of dehydrostearic acid with ricinic acid of melting point $70-73^{\circ}$. *Ethylic ricinate* is an oil which is not hydrolysed by 5 per cent. soda, but when shaken with hydrochloric acid of 20° B., it is converted into polyricinic acids. Acetyl and butyryl derivatives were also prepared.

Oleoricinic acid, $C_{17}H_{33}\cdot COO\cdot C_{17}H_{32}\cdot COOH$, is obtained by allowing a mixture of oleic acid (20 grams), ethylic ricinate (10 grams), and hydrochloric acid of 20° B. (50 grams) to remain for a month. Polyricinic acids are formed:—1, By the action of hydrochloric acid on Turkey-red oils; 2, by the spontaneous decomposition of the acid red oil; 3, by heating ricinic acid with a little ricinosulphuric acid at $105-110^{\circ}$; 4, by the action of hydrochloric acid on ricinic acid and castor oil. Their purity is controlled by means of the cryoscopic method. The remainder of the paper seems to be purely technical. The preparation of red oil from ricinic acid, from castor oil, from oleic acid, and from olein is described.

A. R. L.

Condensation of Alkyl Acetocyanacetates with Phenol.

By A. HELD (*Compt. rend.*, 116, 720—723).—A mixture of ethylic acetocyanacetate and phenol in molecular proportion is added in successive small quantities to an excess of well-cooled concentrated sulphuric acid, allowed to remain in contact at the ordinary temperature for at least 24 hours, and then poured into cold water or over crushed ice. The product crystallises from ether in large, colourless, prismatic crystals melting at 110° ; it is insoluble in water, but dissolves in alcohol, ether, and glacial acetic acid. The alcoholic solution gives an intense red coloration with ferric chloride. The compound has the composition $CON_2H_2\cdot CHAc\cdot COOEt$, and is produced by simple hydration of the ethylic acetocyanacetate. When boiled with the calculated quantity of potassium hydroxide until evolution of ammonia ceases, it yields alcohol and acetic and malonic acids.

In the absence of phenol, sulphuric acid diluted with even a small quantity of water has no action on ethylic acetocyanacetate, but with the concentrated acid, after several weeks' contact, hydration does take place, although to a considerably smaller extent than when phenol is present.

With resorcinol in place of phenol, the results under the same conditions are quite different, and the product is the β -methylumbelliferone

obtained by Pechmann and Duisberg by the action of resorcinol on ethylic acetoacetate in presence of sulphuric acid. In the process of hydration, the nitrogen is eliminated in the form of ammonia.

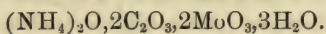
Methylic acetocyanacetate remains unaltered after contact with concentrated sulphuric acid for several weeks at the ordinary temperature, either in presence or absence of phenol. At a higher temperature, it splits up into acetic and carbonic acids, ammonia, and alcohol.

Methylic acetocyanacetate and resorcinol, in presence of sulphuric acid, yield no appreciable quantity of methylumbelliferone, although the fact that the mother liquors, after supersaturation with alkali, show a greenish-blue fluorescence, indicates that some slight change has taken place.

Dehydrating agents other than sulphuric acid, such as zinc chloride or aluminium chloride, gave negative results. C. H. B.

Oxalic acid Derivatives. By A. ROSENHEIM (*Ber.*, 26, 1191—1194).—Tungstic anhydride is dissolved when boiled with potassium oxalate solution; after separation from tungstic acid and evaporation, colourless, crystalline plates are deposited; these have the formula $K_2C_2O_4 \cdot WO_3 + H_2O$, and are decomposed by hydrochloric acid immediately, and by sulphuric acid more slowly. The corresponding *sodium* and *ammonium* salts resemble the potassium salt, but are more readily soluble.

By the action of molybdic anhydride on ammonium oxalate, two salts are obtained; the more readily soluble, $C_2O_4(NH_4)_2 \cdot MoO_3 + H_2O$, can be purified by recrystallisation, when it forms lustrous needles. The second salt, $C_2O_4(NH_4)_2 \cdot 2MoO_3$, crystallises in white crusts, and undergoes decomposition on treatment with hot water. A third salt is prepared by the action of hydrogen ammonium oxalate on molybdic anhydride; it crystallises in prisms, and has the formula



The preceding compounds may also be obtained from hydrogen ammonium oxalate and hydrogen ammonium molybdate. The corresponding *potassium* and *ammonium sodium* salts are crystalline; the *sodium* salts do not crystallise.

A double *ammonium vanadium oxalate*, $3(NH_4)_2O \cdot 4C_2O_3 \cdot V_2O_5 \cdot 4H_2O$, crystallising in long, yellow prisms, is prepared from ammonium oxalate and vanadic anhydride, or from hydrogen ammonium oxalate and ammonium metavanadate. The corresponding *sodium* and *potassium* salts have also been obtained. J. B. T.

Stereochemistry of Malic Derivatives: Variations in the Rotatory Power of Liquids. By A. COLSON (*Compt. rend.*, 116, 818—820).—Acetylmalic acid, obtained by the action of the anhydride on water, melts at 139° , and is very soluble in warm water, 1 part of water dissolving 2 parts of the acid at 50° . Its specific rotatory power lies between -10° and -11° , whatever the degree of concentration of the solution. The author considers that the sign of the

rotatory power is contrary to that which would have been predicted by stereochemical theories.

Acetylmalates are usually soluble in water, but the ferric and silver salts are insoluble. Both the potassium and barium salts are lævogyrate, and the deviation seems to be independent of the base.

Acetylmalic anhydride, obtained by the action of acetic chloride on malic acid, is a white, nacreous substance which melts at 59° . At 60° a layer, 5 mm. in thickness, has a lævorotatory power of $-1^{\circ} 40'$, whilst in superfusion at 25° the deviation falls to $-1^{\circ} 15'$. Contrary to what happens in the case of acetyltartaric anhydride, acetylmalic anhydride has a rotatory power of the same sign as the corresponding acid.

In reply to Aignan (this vol., ii, 354), the author points out that his observations were made with the same compounds as those of Guye.

C. H. B.

Trichloromethanesulphonic Chloride. By T. SELIVANOFF (*J. Russ. Chem. Soc.*, **24**, 333—334).—The substance $\text{CCl}_3\cdot\text{SO}_2\text{Cl}$ is always obtained from carbon bisulphide, and cannot be prepared from trichloromethanesulphonic acid, of which it is supposed to be the acid chloride. The author contends that it is a mixed anhydride of trichloromethanesulphinic acid and hypochlorous acid, adducing the following evidence in support of his contention. The chloride can easily be reduced to the acid $\text{CCl}_3\cdot\text{SO}_2\text{H}$, and is converted by ammonia into the ammonium salt of this acid, $\text{CCl}_3\cdot\text{SO}_2\text{NH}_4$, nitrogen being liberated. The sulphinic acid and hypochlorous acid when mixed do actually give the compound $\text{CCl}_3\cdot\text{SO}_2\text{Cl}$. Ethylamine acts on it with formation of the compounds NEtCl_2 and NEt_2Cl , corresponding with the author's assumption of the presence of hypochlorous acid. Finally, 1 mol. of the chloride $\text{CCl}_3\cdot\text{SO}_2\text{Cl}$ liberates 1 mol. of iodine from a solution of potassium iodide. When boiled for a long time with an aqueous solution of caustic alkali, the chloride does give the alkali salt of trichloromethanesulphonic acid, but this the author attributes to the oxidising action of the alkali hypochlorite simultaneously present in the solution with the salt of the sulphinic acid primarily formed.

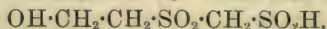
J. W.

Hydrolysis of Sulphones, Sulphonesulphinic Acids, and Sulphinolactones. By E. BAUMANN and G. WALTER (*Ber.*, **26**,

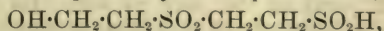
1124—1139).—Both trimethylenedisulphone, $\begin{array}{c} \text{CH}_2\cdot\text{SO}_2 \\ | \\ \text{CH}_2\cdot\text{SO}_2 \end{array} > \text{CH}_2$, and

diethylenedisulphone, $\begin{array}{c} \text{CH}_2\cdot\text{SO}_2\cdot\text{CH}_2 \\ | \\ \text{CH}_2\cdot\text{SO}_2\cdot\text{CH}_2 \end{array}$, in accordance with Stuffer's rule

that sulphones containing sulpho-groups joined to adjacent carbon atoms are capable of being hydrolysed, yield, with baryta-water, hydroxyethylsulphonemethylenesulphinic acid,



and hydroxyethylenesulphonethylenesulphinic acid,



respectively; of these the latter, in accordance with the rule quoted,

can be further hydrolysed; not so the former, which contains two sulpho-groups united to the *same* carbon atom (compare Abstr., 1890, 987). Both these acids yield sulphinolactones which readily oxidise to sulphonolactones, and, in the second case, can be reconverted into the original disulphone.

Trimethylenedisulphone is obtained by condensing formaldehyde with ethylene mercaptan in the presence of alcoholic hydrochloric acid, and oxidising the ethylenemercaptal so formed with permanganate and dilute sulphuric acid. It forms rhombic tables melting at 204—205°, and yields a *dichloro-* and a *dibromo-derivative* (melting with decomposition at 222—223° and 271° respectively), the two hydrogen atoms of the methylene group in $\text{SO}_2\cdot\text{CH}_2\cdot\text{SO}_2$ being replaced. By warming the sulphone with baryta-water, *hydroxyethylsulphonemethylenesulphinic acid* is formed as the *barium salt*; the *potassium salt* was also prepared. The acid itself is a syrup which when heated in aqueous solution loses sulphurous anhydride and yields *hydroxyethylmethylsulphone*, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\text{Me}$, as a colourless, crystalline mass which melts at 20.5°, and is oxidised by chromic acid to *methylsulphoneacetic acid*, $\text{COOH}\cdot\text{CH}_2\cdot\text{SO}_2\text{Me}$; this, when heated, yields methylsulphone. A concentrated solution of the sulphinic acid, when allowed to evaporate spontaneously, gradually deposits quadrangular prisms of the *sulphinolactone*; this melts at 164°, and is oxidised by acid permanganate in the cold to the corresponding *sulphonolactone*, which forms hexagonal prisms, turns brown at 170°, and melts at 206—207°.

Diethylenedisulphone, obtained by oxidising diethylene bisulphide with acid permanganate, is converted by heating with baryta-water into *hydroxyethylsulphonethylenesulphinic acid*. On boiling the *barium salt* with water, it is partially reconverted into diethylenedisulphone; the *copper salt* was also prepared. The acid itself, in concentrated aqueous solution, forms a syrup which solidifies slowly, more quickly when warmed, to a crystalline mass of the *lactone*; this crystallises in needles which turn yellow at 190—200°, and melt with decomposition at 220—222. This lactone, when boiled with a few drops of aqueous sodium carbonate, is only partially reconverted into the sulphinic acid; the rest of it yields diethylenedisulphone. When oxidised with acid permanganate, it yields the corresponding *sulpholactone*, as needles or hexagonal plates which become discoloured at 220°, melt with decomposition at 255—256°, and with baryta-water yield the *barium salt* of the corresponding *sulphonic acid*. The *potassium* and *silver salts* of this acid were also prepared; the acid itself is a syrup which cannot be reconverted into its lactone. When hydroxyethylsulphonethylenesulphinic acid is boiled for several days with baryta-water, it is hydrolysed, forming, for the most part, glycol and ethylenedisulphonic acid, $\text{SO}_2\text{H}\cdot\text{CH}_2\text{CH}_2\cdot\text{SO}_2\text{H}$, but also, to a slight extent, the other possible product, hydroxyethylsulphinic acid, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\text{H}$. The latter could not be isolated, but a substance, *diethylene oxide sulphone*, $\text{O} \begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix} \text{SO}_2$, was obtained, and this probably resulted from condensation of hydroxyethylsulphinic acid with glycol; it forms colourless plates, melts at 130°,

and volatilises unchanged. *Ethylenesulphinic acid* was obtained in the form of its *barium* and *silver salts*; the former, when oxidised with bromine water, yields the *barium salt* of the corresponding *disulphonic acid* as colourless prisms; when it is converted into the sodium salt, and the latter heated at 100° with ethylic iodide in dilute alcohol, *ethylenediethylsulphone*, $\text{SO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\text{Et}$, melting at 136° , is obtained.

C. F. B.

Hydrogenisation of Benzene. By N. KIJNER (*J. Russ. Chem. Soc.*, **24**, 450—454).—Benzene (1 c.c.) was heated for 24 hours at 260 — 270° with hydriodic acid (25 c.c.) of sp. gr. 1.97. Some of the benzene remained unchanged, but the bulk was converted into hexahydrobenzene, no intermediate substances being formed. The further reduction to hexane is incomparably more difficult, for even after heating hexahydrobenzene for 35 hours with the same acid at 275 — 298° , only about a fifth part is converted into the saturated hydrocarbon.

J. W.

Formation of Nitro-derivatives at Low Temperatures. By R. PICTET (*Compt. rend.*, **116**, 815—817).—At very low temperatures, the action of the ordinary nitrating mixture of sulphuric and nitric acids is materially modified. If a mixture of concentrated nitric and sulphuric acids is cooled to -55 — -65° , and mixed with successive small quantities of finely powdered naphthalene, also cooled to -65° , and the vessel is placed in a receptacle cooled to -110 — -120° , no action takes place below -60° , but if the sparks from a powerful Ruhmkorff coil are allowed to impinge on the liquid, reaction begins. At -50 — -55° the action begins without the aid of the spark, and hence -60° seems to be the limiting temperature of this reaction. Under these conditions the proportion of β -dinitronaphthalene formed is much higher than at the ordinary temperature. An average result is β -dinitronaphthalene, 46 per cent., α -nitronaphthalene, 22.7 per cent., and α -dinitronaphthalene, 31.3 per cent.

The use of low temperatures makes it possible to determine and utilise the direction of the maximum tendency of the chemical affinities of the constituents.

At -55° the weight of paranitrotoluene obtained by the direct nitration of toluene is 5.5 times as great as at 0° , and it follows that the para-group corresponds with the primary affinities of the constituents.

The limiting temperature for the nitration of phenol without the aid of the spark is -65° . By allowing the spark from a coil to play on the mixture, complete reaction can be produced without any apparent rise of temperature if the receptacle in which the vessel is placed is kept at from -110 — -120° . At -65° the weight of paranitrophenol obtained is five times as great as at -40° .

When converting dinitrobenzene into metanitriline by the action of hydrogen sulphide in presence of ammonia, and then diazotising the metanitriline, about double the yield is obtained by conducting all the operations at low temperatures.

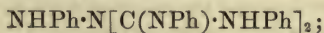
C. H. B.

Constitution of the Dihydroxythiobenzenes. By G. TASSINARI (*Gazzetta*, **23**, i, 191—196; compare *Abstr.*, 1892, 1316).—On nitrating diphenylsulphone and reducing the product, diamidodiphenylsulphone is formed; this is diazotised and treated with mercuric chloride. On boiling the double salt thus obtained with water, it yields a dihydroxydiphenylsulphone, which forms colourless needles melting at 190—191°, and is necessarily a meta-derivative. The author finds it to be identical with the sulphone obtained by oxidising the dihydroxythiobenzene melting at 130° (*Real. Accad. Linc.*, **4**, 47); the latter is hence a meta-derivative, and in the reaction between chloride of sulphur and parabromophenol, the sulphur enters the molecule in the ortho-position to the bromine. The author was unable to prepare orthodihydroxythiobenzene by reducing dibromodinitrothiobenzene with hydriodic acid or tin and hydrochloric acid (compare Purgotti, this vol., i, 330).
W. J. P.

Bülow's Reaction and the Oxidation of Hydrazones. By H. v. PECHMANN (*Ber.*, **26**, 1045—1047).—By the action of amylic nitrite on benzaldehydephenylhydrazone in ethereal solution, a tetrazone, $\text{CHPh}\cdot\text{N}\cdot\text{NPh}\cdot\text{NPh}\cdot\text{N}\cdot\text{CHPh}$, is formed; this crystallises from benzene in yellow needles, melts at 190°, and gives an intense blue colour with concentrated sulphuric acid. By the action of phenylhydrazine on the tetrazone, benzaldehydephenylhydrazone is regenerated. The compound is also formed by the mutual action of nitrosophenylhydrazone and benzaldehyde, and has already been obtained by Minunni (this vol., i, 97) by the oxidation of benzaldehydephenylhydrazone with mercuric oxide; he erroneously states the melting point to be 179—180°. The formation of the above tetrazone is analogous to that of osotetrazones from osazones; Bülow's test for hydrazones depends on the formation of a tetrazone and its subsequent reaction with sulphuric acid.

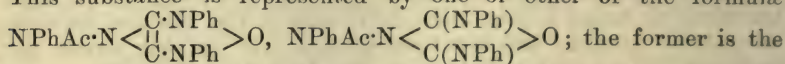
The author points out the advantages of amylic nitrite as an oxidising agent, particularly where the presence of moisture is undesirable.
J. B. T.

Wessel's Dicarbo-base from Phenylhydrazine and Carbodiphenylimide and its Cyclic Decomposition Products. By C. SCHALL (*Ber.*, **26**, 1180—1191).—Wessel's dicarbo-base (*Abstr.*, 1888, 1083) is readily prepared by fusing diphenylguanidine (2 mols.) with phenylhydrazine (1 mol.) for five minutes, ammonia being evolved; it is probably represented by the formula



and should accordingly be termed *α-bis-diphenylformamidylphenylhydrazine*, the complex $\text{C}(\text{NPh})\cdot\text{NPh}$ being designated *diphenylformamidyl* (compare Markwald and Wolff, this vol., i, 25); the base, if prepared from technical materials, is purified by treatment with concentrated hydrochloric acid at 150°, and melts at 204°, instead of 200°, as stated by Wessel; on heating with hydrochloric acid at 200°, it is completely decomposed, aniline being formed; it reacts with phenylthiocarbimide, but the product is difficult to purify.

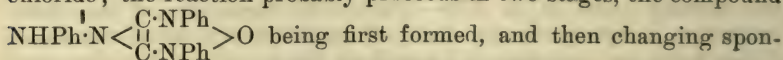
The *acetyl derivative*, $\text{NPhAc}\cdot\text{N}[\text{C}(\text{NPh})\text{NHPPh}]_2$, is prepared by the action of acetic anhydride on the base at 130° , and crystallises in slender, silky, lustrous needles melting at 174° . By the action of acetic anhydride at 200° on the acetyl derivative, or by treatment with benzoic anhydride and soda, a compound is obtained, together with acetanilide or benzanilide, which crystallises from alcohol in colourless, transparent, hexagonal laminæ, melts at 170° , and may be distilled under reduced pressure without decomposition. This substance is represented by one or other of the formulæ



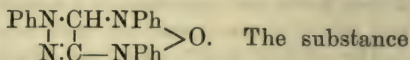
the former is the more probable, as the reduction product does not show strongly marked basic properties (see below). A molecular weight determination by Raoult's method confirms the above formula. The compound does not react with phenylthiocarbimide, carbon bisulphide, or alkalis. The *tribromo-derivative*, $\text{C}_{20}\text{H}_{12}\text{N}_4\text{OAcBr}_3$, crystallises in slender needles, and melts at $224\text{--}225^\circ$.

By the action of nitric acid on the compound $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_2$ (m. p. 170°), the acetyl group is eliminated, and a nitro-derivative, $\text{C}_{20}\text{H}_{15}\text{N}_4\text{O}\cdot\text{NO}_2$, is obtained, which crystallises in colourless, slender needles, melts at $197\cdot5^\circ$, volatilises without decomposition at 272° , and becomes pale red on exposure to air.

On heating the compound (m. p. 170°) with hydrochloric acid at $150\text{--}180^\circ$, the acetyl group is also eliminated, and a substance is formed which crystallises in long, silky, lustrous needles, melts at 161° , is unaltered at 300° , and gives a blue coloration with acetic chloride; the reaction probably proceeds in two stages, the compound



being first formed, and then changing spontaneously into the isomeride

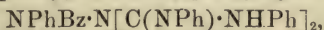


The substance does not react with hydroxylamine hydrochloride, phenylhydrazine, or phenylthiocarbimide at 150° ; by the action of hydriodic acid and phosphorus at 150° , or of hydrochloric acid at 275° , aniline is formed. Benzoic anhydride appears to yield an *additive compound*, which crystallises in thick, colourless plates, and is decomposed by recrystallisation from acetic anhydride at $220\text{--}230^\circ$, the acetyl derivative being probably regenerated. The *picrate*, $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}(\text{C}_6\text{H}_5\text{N}_3\text{O}_7)_2$, is unstable and crystalline. The *dibromo-derivative* is formed by the action of bromine at ordinary temperatures, and melts at 178° ; the *tribromo-compound* is obtained on heating with bromine in acetic acid solution; it crystallises in needles, melts at 227° , and decomposes at 300° . Two nitro-compounds have been prepared; the trinitro-derivative, $\text{C}_{20}\text{H}_{13}\text{N}_4\text{O}(\text{NO}_2)_3$, is formed at ordinary, the dinitro-derivative, $\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}(\text{NO}_2)_2$, at higher, temperatures; the first crystallises from nitrobenzene in orange needles, softens at $291\text{--}295^\circ$, and melts at 363° ; the second is deposited from acetic acid in red plates, and from nitrobenzene in nodular aggregates, which melt at 253° .

On reducing the acetyl compound, $\text{C}_{22}\text{H}_{18}\text{N}_4\text{OAc}$ (m. p. 170°), with sodium in amyl alcoholic solution, a neutral substance, which

melts at 218—219°, is obtained, together with ammonia, aniline, and in small quantity an oily base.

β-Benzoyl-α-bis-diphenylformamidylphenylhydrazine,



is prepared from benzoic anhydride and the dicarbo-base, and crystallises in slender needles melting at 149°. On treatment with soda, benzanilide is eliminated, and a compound, $\text{C}_{20}\text{H}_{15}\text{N}_4\text{OBz}$, is formed, which is deposited in hexagonal needles melting at 172°. It does not combine with picric acid; by the action of hydrochloric acid, the benzoyl group is eliminated, and the compound (m. p. 161°) described above is formed. The *bromo-derivative*, $\text{C}_{20}\text{H}_{14}\text{BrN}_4\text{OBz}$, melts at 154°. The *dinitro-derivative*, $\text{C}_{20}\text{H}_{13}\text{N}_4\text{O}(\text{NO}_2)_2\text{Bz}$, crystallises with 1 mol. of acetic acid, melts at 130°, decomposes at 131—136°, resolidifies at 140°, and finally melts at 200°.

The author explains the action of benzoic or acetic anhydride on bis-diphenylformamidylphenylhydrazine by assuming that an additive compound, $\text{NPh} \cdot \text{N} < \begin{smallmatrix} \text{C}(\text{NPh}) \cdot \text{NPh} \cdot \text{OR} \\ \text{C}(\text{NPh}) \cdot \text{NPh} \cdot \text{R} \end{smallmatrix}$, is first formed (R = Ac or Bz); substitution then takes place, and the additive compound is decomposed by alcohol; in presence of soda, the action proceeds further, and the group NPhR is eliminated.

Bis-diphenylformamidylphenylhydrazine yields a *dimethyl derivative*, $\text{NPh} \cdot \text{C}(\text{NPh}) \cdot \text{N}(\text{NMePh}) \cdot \text{CMe} \cdot \text{NPh}$, which forms an unstable, yellow powder melting at 227—232°, with decomposition; the *hydrochloride* is also unstable; the *hydriodide* occurs in two modifications melting at 258—260°; the one crystallises from alcohol in yellow needles, the other forms white plates, and is converted into the yellow compound by fusion, or by solution in glacial acetic acid; it does not dissolve in any other medium. J. B. T.

Hippurylphenylbuzylene; New Synthesis of Azoimide. By T. CURTIUS (*Ber.*, 26, 1263—1271).—It is reasonable to suppose that when diazobenzene reacts with hydrazine, the two substances first unite to form a compound, $\text{NPh} \cdot \text{N} \cdot \text{NH} \cdot \text{NH}_2$, and this then breaks up in two ways, yielding in one case diazobenzenimide and ammonia, in the other, aniline and azoimide. As a matter of fact, this does take place, but the intermediate compound cannot be isolated; the four decomposition products were, however, obtained, the last two in amount corresponding with only 10 per cent. of the theoretical.

An intermediate product is, however, obtained when cooled aqueous solutions of diazobenzene sulphate and hippurylhydrazine are mixed, and separates out in almost colourless, crystalline plates. It has the constitution $\text{NPh} \cdot \text{N} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NHBz}$, and is named *hippurylphenylbuzylene*. It melts at 86°, and is instantaneously decomposed by aqueous alkalis or alkali carbonates, or by dilute acids, yielding chiefly diazobenzenimide and hippuramide, but also aniline and the decomposition products of diazohippuramide, namely, azoimide and hippuric acid.

From diazobenzene sulphate and benzoylhydrazine, *benzoylphenylbuzylene*, $\text{NHBz} \cdot \text{NH} \cdot \text{N} \cdot \text{NPh}$, is obtained in a similar manner as a

colourless, crystalline precipitate; it decomposes partially while it is being filtered and dried, yielding diazobenzenimide and benzamide, with some aniline and benzoylazoimide.

C. F. B.

Basic Bye-product obtained on benzylating Acetoxime. By E. BECKMANN and A. KÖSTER (*Annalen*, **274**, 37—41).—Beckmann, when benzylating acetoxime (*Ber.*, **22**, 439), obtained a bye-product melting at 122—123°. The authors find that it is $\beta\beta$ -dibenzylhydroxylamine, and attribute its formation to the setting free of a small quantity of hydroxylamine during the reaction.

A. R. L.

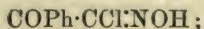
Spectrophotometric Investigation of Salts of Aromatic Bases. By L. MEYER (*Zeit. physikal. Chem.*, **11**, 426—428).—A note to the paper by Weigle on the above subject (this vol., i, 333). The author shows that if the rosaniline salts are regarded not as hydrochlorides of amines, but as chlorides of amido-alcohols, the results of Weigle's investigations would still be in keeping with this view.

H. C.

Constitution of the Mauveïnes. By O. FISCHER and E. HEPP (*Ber.*, **26**, 1194—1196).—The simplest mauveïne, termed by Perkin pseudomauveïne and by the authors phenomauveïne, is identical with the violet induline obtained by the action of nitrosoaniline on aniline hydrochloride, and also with B₂-4-anilidoinduline from diphenylmetaphenylenediamine and nitrosoaniline (compare this vol., i, 335); the corresponding dimethylphenomauveïne is the "indazine" prepared from nitrosodimethylaniline and diphenylmetaphenylenediamine, whilst the mauvindone, $C_6H_3O \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ \text{---} \quad \text{---} \\ N_{Ph} \end{smallmatrix} C_6H_3 \cdot NHPH$, is formed from nitrosophenol and diphenylmetaphenylenediamine, and closely resembles the rosindones. The great similarity in properties between the mauveïnes and safranines renders it probable that the amido-groups are symmetrically distributed in both classes of compounds. The authors have hitherto failed in preparing specimens of safranine bases free from oxygen.

J. B. T.

Action of Chlorine on Isonitrosoketones. By L. CLAISEN and O. MANASSE (*Annalen*, **274**, 95—98).—In the preparation of isonitrosoketones by treating the ketone with amylic nitrite and nitrous acid (*Abstr.*, 1889, 585), an excess of hydrochloric acid must be avoided or a chlorinated derivative is obtained. From acetophenone, for example, there is produced *chlorisonitrosoacetophenone*,



it forms nacreous plates, melts at 132°, and yields benzoic acid on decomposition with alkalis. In an analogous manner, by chlorinating acetone, Glutz's chlorisonitrosoacetone, $COMe \cdot CCl \cdot NOH$, melting at 109°, is formed.

A. R. L.

Aromatic Alkyl Ketones. By A. CLAUS (*J. pr. Chem.* [2], **47**, 420—425; compare this vol., i, 162).—*Orthocymylmethylketoxime* [Pr^a : Me : CMe·NOH = 3 : 4 : 1] is a viscid, yellow oil.

Orthocymylcarboxylic acid [$\text{Me} : \text{Pr}^a : \text{COOH} = 1 : 2 : 4$] is distilled over with steam from the product of the oxidation of orthocymyl methyl ketone (Abstr., 1890, 770) by dilute permanganate solution in the cold; it forms small, colourless crystals, melts, but not sharply, at 89° , dissolves in the usual solvents, and sublimes. The *barium* salt (with $2\text{H}_2\text{O}$), the *calcium* salt (with $2\text{H}_2\text{O}$), and the *silver* salt were prepared.

Orthocymylacetamide [$\text{Me} : \text{Pr}^a : \text{CH}_2\cdot\text{CONH}_2 = 1 : 2 : 4$] crystallises in white needles, and melts at 112° ; by hydrolysis, it yields *methylpropylphenylacetic acid* [$\text{Me} : \text{Pr} : \text{CH}_2\cdot\text{COOH} = 1 : 2 : 4$], a viscid, yellow oil; the *calcium* and *barium* salts (each with 1 mol. H_2O) have been prepared.

Orthocymyl ethyl ketone [$\text{Me} : \text{Pr}^a : \text{COEt} = 1 : 2 : 4$] is a colourless liquid of aromatic odour which boils at $266\text{--}269^\circ$. *Orthocymyl propyl ketone* [$\text{Me} : \text{Pr}^a : \text{COPr}^a = 1 : 2 : 4$] is a colourless oil which boils at $285\text{--}287^\circ$. The *ketoxyms* of these two ketones are viscid, uncrystallisable oils.

A. G. B.

Isomeric Amidobenzoic acids. By O. DE CONINCK (*Compt. rend.*, 116, 758—760).—The coefficients of solubility of the three isomerides in pure ether are as follows:—

	Ortho.	Meta.	Para.
At 2.7°	1.0840	0.1700	0.6414
At $5.6\text{--}6.8^\circ$	1.6050	0.1810	0.8210

and in alcohol of 90°

At 3.0°	0.8130	0.1790	0.8400
At 9.6°	1.0700	0.2200	1.1300

The coefficient of solubility of metamidobenzoic acid in dilute ethyl alcohol (1 : 3) at 14.9° is 0.0726, at 16.8 , 0.0734; in alcohol of 90° at 12.5° , 0.2920; in methyl alcohol at 10.5° , 0.4046; in acetone at 11.3° , 0.6215; in methylic iodide at 10° , 0.0040; in ethylic iodide at 0° , 0.0016; in chloroform at 12° , 0.0070; in bromoform at 8° , traces; in terebenthene at 10° , traces; in water at 0° , 0.0403; at 20° , 0.0686; at 28° , 0.0820; at 38° , 0.1010; at 48.1° , 0.1396; at 54° , 0.1580; at 67° , 0.2870. A table is given showing the coefficient of solubility of the acid in water at various temperatures between 0.0° and 67.0° . Metamidobenzoic acid is easily soluble in methyl alcohol and in acetone, but almost insoluble in alcohol derivatives and in aromatic hydrocarbons.

C. H. B.

Alkyllic Benzeneazocyanacetates and their Analogues. By A. HALLER and E. BRANCOVICI (*Compt. rend.*, 116, 714—718).—Ethylic and methylic benzeneazocyanacetates, after being treated with alkali hydroxides at the ordinary temperature, show considerable differences in appearance and properties. This fact has already been observed by Kruckeberg in the case of the ethylic salt.

Ethylic benzenazocyanacetate α , obtained by the action of an alcoholic solution of ethylic sodiocyanacetate on a cooled aqueous solution of diazobenzene chloride, dissolved in excess of potassium

hydroxide, precipitated by means of sulphuric acid and crystallised from alcohol, forms yellow needles melting at 124—125°, and having all the properties previously described.

If the product is crystallised from alcohol or benzene without being previously dissolved in potassium hydroxide solution, it forms needles which melt at temperatures varying from 104° to 120°. After dissolving in potash solution and reprecipitating with acid, however, the product melting at 124—125° is always obtained.

Ethylic benzeneazocyanacetate β , obtained by Kruckeberg by exactly neutralising an acetic or hydrochloric acid solution of the α -modification, or by heating the α -modification at 130°, is always formed at the same time as the α -variety, although in much smaller quantity, and when the crude product is repeatedly crystallised from alcohol, the β -modification accumulates in the mother liquors. It is also obtained by incompletely neutralising an alkaline solution of the α -modification, or by heating the latter for several hours in a xylene solution, or for several days at 100°. The β -modification crystallises from alcohol in rhomboidal tables melting at 85°; it is much more soluble than the α -modification in most of the ordinary solvents. From benzene it crystallises in hexagonal lamellæ, which are transparent while in the liquid, but become opaque in contact with air. When dissolved in potassium hydroxide and reprecipitated with excess of acid, it is converted into the α -modification.

Ethylic benzoylbenzeneazocyanacetate is obtained by the action of benzoic chloride on a solution of the α -modification of the preceding compound in sodium hydroxide; it crystallises from alcohol in white needles melting at 158°. Ethylic methylbenzeneazocyanacetate is obtained by the action of methylic iodide on either form of the first compound; it crystallises in pale-yellow prisms melting at 57°. Ethylic sodiobenzenazocyanacetate is obtained by evaporating a mixture of sodium ethoxide and ethylic benzeneazocyanacetate in molecular proportion. It forms a crystalline, yellow powder soluble in water or in alcohol, but insoluble in alkalis. When dried in the air, it has the composition $C_{11}H_{10}N_3O_2Na + 2H_2O$, but loses part of its water in a vacuum.

Methylic benzeneazocyanacetate, obtained in the same way as the ethylic salt, forms an α -modification which melts at 141°, and is very slightly soluble in benzene, but more soluble in boiling alcohol, which partially converts it into the β -modification. The latter crystallises in yellow lamellæ or needles melting at 115°.

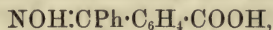
Methylic methylbenzeneazocyanacetate melts at 121°, and methylic benzoylbenzeneazocyanacetate crystallises from benzene in slender, white needles melting at 147°.

These compounds do not give reactions characteristic of hydrazones. The differences between the α - and β -modifications are most probably due to stereoisomerism.

C. H. B.

Action of Hydroxylamine on Orthobenzoylbenzoic acid.
By F. H. THORP (*Ber.*, 26, 1261—1263).—When orthobenzoylbenzoic acid is heated at 130° with hydroxylamine hydrochloride in absolute alcohol, there is obtained not an oxime, but phthalanilic acid, formed

from the oxime by a molecular transformation similar to that observed by Beckmann (Abstr., 1886, 618; 1887, 826). When this acid is sublimed, it loses water and yields phthalanil, $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{NPh}$, which crystallises in long needles, melts at 203° , and is hydrolysed into phthalic acid and aniline hydrochloride by heating at 130° with strong hydrochloric acid. *Orthobenzoylbenzoic acid oxime*,

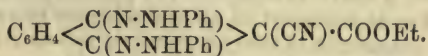


may, however, be obtained by allowing the acid to remain with hydroxylamine hydrochloride in dilute alcohol for a long time at the ordinary temperature, and finally warming the mixture on the water-bath. It forms long needles melting at $159\text{--}160^\circ$, and, when hydrolysed, yields the same products as phthalanil. C. F. B.

Homoterephthalic acid. By M. FILETI and G. BALDRACCO (*J. pr. Chem.* [2], 47, 532—534).—The authors have prepared homoterephthalic acid by the hydrolysis of paracyanobenzyl cyanide (Mellinghoff, Abstr., 1890, 239), and find that, when thus prepared, it is in every respect identical with the homoterephthalic acid obtained by oxidising homocumic acid (Abstr., 1891, 1057), melting at $237\text{--}238^\circ$, not $285\text{--}288^\circ$ as given by Mellinghoff. During the hydrolysis a substance, sparingly soluble in water, was isolated in the form of a crystalline powder melting at 281° . A. G. B.

Ethylic Phthalocyanacetate. By P. T. MULLER (*Compt. rend.*, 116, 760—763).—The white product melting at 175° , obtained by the action of phthalic chloride on ethylic sodiocyanacetate (Abstr., 1891, 1337), is a mixture of two ethylic phthalocyanacetates, the one melting at $140\text{--}141^\circ$, the other at $190\text{--}192^\circ$. They can be separated by fractional crystallisation from benzene or chloroform, in which the more fusible compound is the more soluble. Apart from differences in melting point and solubility, the two modifications have the same properties, and they are, undoubtedly, stereoisomerides.

Ammonia converts ethylic phthalocyanacetate into symmetrical phthalamide at the ordinary temperature, and this melts at 219° with evolution of ammonia and formation of phthalimide. If only a small quantity of ammonia acts on the phthalocyanacetate, phthalimide melting at 228° is obtained at once. With a benzene solution of phenylhydrazine, ethylic phthalocyanacetate yields a dihydrazone melting at 149° : it has the constitution



Ethylic phthalocyanacetate dissolves very slowly, but completely, in sodium carbonate solution, and, if the liquid is treated with excess of dilute sulphuric acid, *ethylic orthocarboxybenzoylcyanacetate*, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{COOEt}$, is precipitated, and can be crystallised from ether; it melts at $121\text{--}122^\circ$, and, when boiled with water, yields phthalic acid and ethylic cyanacetate. It is a bibasic acid, and can be titrated with sodium hydroxide solution, using

phenolphthaleïn as indicator; it yields a white, amorphous diargentate salt. A whole series of alkyl hydrogen salts of this compound can be obtained by the action of ethylic phthalocyanacetate on solutions of sodium alkyl oxides in the corresponding alcohols. They have the general formula $\text{COOR} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{COOEt}$, and are insoluble in water, but dissolve in the ordinary organic solvents. They are monobasic acids, and can be titrated with sodium hydroxide solution, using phenolphthaleïn as indicator. Their lead salts are white, silver salts white or rose-coloured, and copper salts pale green. With ferric chloride, they yield a reddish-brown precipitate which dissolves in ether forming a beautiful red solution. This reaction is characteristic of the group $\text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{COOEt}$. The *methylic* salt melts at $64-65^\circ$, its *silver* salt is white; the *ethylic* salt is viscous, and its silver salt is rose-coloured; the *propylic* salt melts at $69-70^\circ$, and its silver salt is reddish; the *benzylic* salt is crystalline, and melts at 74° . The above alkylic salts, when boiled with a large excess of water, yield *orthocyanacetophenonecarboxylic acid*, $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CN}$, a crystalline powder melting at $136-138^\circ$.

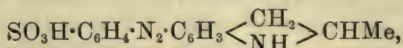
Almost all these reactions are quantitative. Ethylic phthalocyanacetate sometimes behaves as a symmetrical, sometimes as an unsymmetrical compound. It would seem that certain parts of the molecule have a degree of mobility such that, under different conditions, it can take up the orientation required to produce at once the most stable molecule, which is sometimes symmetrical, sometimes unsymmetrical.

C. H. B.

Dihydromethylketole. By E. BAMBERGER and E. A. ZUMBRÖ (Ber., 26, 1285—1291).—Dihydromethylketole, $\text{C}_6\text{H}_4 \langle \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \end{smallmatrix} \rangle \text{CHMe}$, or methyl dihydroindole, is, as the sequel shows, precisely analogous in chemical character to tetrahydroquinoline, $\text{C}_6\text{H}_4 \langle \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{NH}_2 \cdot \text{CH}_2 \end{smallmatrix} \rangle$; this character is therefore independent of the length of the side ring, and we have here a case of "alicyclic homology" comparable with the homology of fatty hydrocarbons. This is not the case with the corresponding non-hydrogenised substances; indole, for example, behaves very differently from quinoline.

Diazoamidodihydromethylketole, $\text{C}_6\text{H}_4 \langle \begin{smallmatrix} \text{CH}_2 \\ \text{N}(\text{N}_2\text{Ph}) \end{smallmatrix} \rangle \text{CHMe}$, is formed from diazobenzene and dihydromethylketole. It crystallises in long, hard, yellowish, glassy, monoclinic (?) prisms, melts at 51.5° , and exhibits the typical reactions of diazoamido-compounds; in alcoholic solution, acids transform it into an isomeric red azo-dye.

Hydromethylketoleparazobenzenesulphonic acid,



is formed when hydromethylketole is mixed with diazosulphanilic acid. It is obtained in two forms: as violet needles, insoluble in water, and melting above 260° , and as a green mass with red streak, soluble in water. The first variety is formed in larger amount in

concentrated solution and when the free base is used; the second in dilute, slightly acid solution. Both varieties, when heated with hydrochloric acid and stannous chloride, yield sulphanilic acid and *paramidodihydromethylketole*, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \end{smallmatrix} > \text{CHMe}$; the latter forms white, glassy needles melting at 93.5° : its *hydrochloride*, white, crystalline flakes. Like *paramidotetrahydroquinoline*, the base itself yields the colour reactions of *paraphenylenediamine*. C. F. B.

Indoxazen Derivatives. By V. MEYER, O. LUST, J. MARCUSSEN, and W. A. BONE (*Ber.*, 26, 1250—1257; compare *Abstr.*, 1892, 992, and this vol., i, 94, 35).—Phenylindoxazen, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CPh} \\ \text{O} \end{smallmatrix} > \text{N}$, may be prepared from *orthonitrobenzophenone oxime* by boiling it with aqueous soda, sodium nitrite being also formed.

When *orthonitrophenylglyoxylic acid oxime* is boiled with water, carbonic anhydride is evolved, and *orthonitrobenzonitrile* is formed. If aqueous sodium carbonate be used, the nitro-group is displaced by hydroxyl, and *salicylonitrile* is produced: whilst if aqueous soda is used, the cyano-group is also attacked and hydrolysed, and *salicylic acid* is formed.

Similarly, if *nitro-ortho-chlorobenzaldoxime* is boiled with aqueous soda, *nitrosalicylic acid* is formed, whilst if aqueous sodium carbonate is used, *nitrosalicylonitrile* is produced; the latter may also be obtained by nitrating *salicylonitrile* with concentrated nitric acid at 15° ; it forms yellow needles melting at 190° . If fuming nitric acid is used, a *dinitrosalicylonitrile* $[\text{CN} : \text{OH} : (\text{NO}_2)_2 = 1 : 2 : 3 : 5]$ is formed; it crystallises in yellow tables melting at 175° .

Meta- and para-bromobenzophenone oximes yield no substances analogous to the indoxazen obtained from the ortho-derivative.

C. F. B.

Preparation of Benzidine Sulphate. By H. TEICHMANN (*Zeit. angew. Chem.*, 1893, 67).—A mixture of nitrobenzene (100 grams) sodium hydroxide solution (sp. gr. 1.4; 80 grams) and water (500 c.c.) is heated in a reflux apparatus on the water-bath; zinc-dust (160 grams) is then introduced in small portions; during the addition, which extends over 6—8 hours, the mixture is agitated. When cold, the product is gradually poured into hydrochloric acid (sp. gr. 1.2; 1500 c.c.), which should be free from arsenic, the temperature being kept low by the addition of ice. After this, the liquid is heated to boiling by passing in a current of steam, and it is filtered from resinous matter while hot. The hot filtrate is then treated with a saturated solution of sodium sulphate, whereby almost the whole of the benzidine is precipitated as sulphate. It is collected, washed with water, and dried, when it is obtained in the form of a greyish-blue powder; the yield is 90 per cent. of the weight of nitrobenzene employed, and the product contains 2.5 per cent. of ash. About 5 grams of aniline is driven over by passing a current of steam into the reduction product, but only a relatively small quantity of diphenylamine is formed.

A. R. L.

Preparation of Benzidine. By E. ERDMANN (*Zeit. angew. Chem.*, 1893, 163—164).—Commenting on Teichmann's method (last abstract), the author describes a process for the preparation of benzidine on a large scale which he states is quicker, and gives a good yield. A mixture of nitrobenzene (2 kilos.), sodium hydroxide solution (40° B., 6 litres), water (2 litres), and alcohol (1 litre) is introduced into an earthenware cylinder furnished with a side tube, and a lid having a hole to admit an iron or wooden mixer. The alcohol is not absolutely necessary, but the reaction proceeds with greater regularity when it is used, and less aniline is formed. The side tube is attached to a condenser, and zinc-dust (3·4 kilos.) is introduced in small portions through a tube issuing from the lid. An energetic reaction soon sets in, and a mixture of alcohol and nitrobenzene distils over, which is repeatedly returned. The addition of zinc-dust is so regulated that the mixture does not froth over, and it is kept in agitation with the mixer; when these precautions are neglected, the reaction may become sufficiently violent to cause explosion; the reduction is complete in 2½ hours. The product is allowed to cool, and on the following day diluted with water and thrown upon a sieve, which allows the zinc oxide to pass through, but retains the crystals of hydrazobenzene; the hydrazobenzene may also be isolated by dissolving the zinc oxide at 10—15° in concentrated hydrochloric acid (18 litres). The yield is hydrazobenzene 1170 grams, benzidine 128 grams, and aniline 18 grams. To convert hydrazobenzene into benzidine, 500 grams of the former is boiled with concentrated hydrochloric acid (800 c.c.) and water (1 litre); the precipitated benzidine hydrochloride is collected, and dilute sulphuric acid added to the filtrate as long as a precipitate falls, which is collected. The filtrate is rendered faintly alkaline, the aniline driven over, and the semi-oily residue of diphenylamine collected, converted into sulphate, and further purified. The diphenylamine represents 8—10 per cent. of the hydrazobenzene employed. The yield of benzidine does not exceed 50 per cent. of the weight of nitrobenzene reduced. Boiling water dissolves 0·011 part, and cold water 0·0004—0·0005 part of benzidine. A. R. L.

Formation of Acridine Dyes. By R. MÖHLAU and E. FRITZSCHE (*Ber.*, 26, 1034—1044).—*Hexamethyltriamidophenylacridine*, $C_{25}H_{28}N_4$, is prepared by the action of hydrochloric acid on nitrosodimethylaniline hydrochloride and dimethylaniline; the addition of paraformaldehyde is advantageous; the mother liquor contains dimethylamine, paramidophenol, and chloroparamidophenols. The compound has been previously described (*Ber.*, 16, 2729) as "rubifuchsine," $C_{16}H_{19}N_3$; it is readily soluble in dimethylaniline, and crystallises in stellate groups of golden, flat needles, or plates, which melt at 270°. On distillation, the greater part of the compound decomposes into paraphenylenediamine and dimethylparatoluidine. The *hydrochloride*, $C_{24}H_{28}N_4 \cdot 2HCl$, is deposited in small, light red needles, containing $1H_2O$; on slowly cooling the solution, brownish-red or steel-blue needles are formed, containing $5H_2O$; the anhydrous

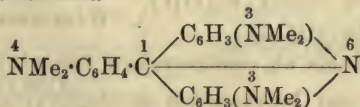
salt is red, and gives a colourless solution with concentrated hydrochloric acid or sulphuric acid.

On reducing the dye with zinc-dust in acetic acid solution, a colourless, readily oxidisable leuco-derivative is formed; in hydrochloric acid solution, the base is resolved into paraphenylenediamine, dimethylparatoluidine, and, probably, benzene.

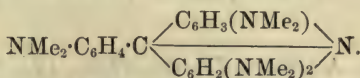
Octomethyltetramidophenylacridine, $C_{27}H_{33}N_5$, is obtained together with the hexamethyl compound, and is readily prepared by the action of hydrochloric acid on a mixture of paraformaldehyde, dimethylaniline, and nitrosodimethylaniline hydrochloride; the base crystallises from alcohol in yellow plates, melts at 229° , and in small quantities distils without decomposition. The compound gives no coloration with concentrated hydrochloric acid or sulphuric acid; on continuous dilution, the solution becomes yellow, then orange-red. The *hydrochloride*, $C_{27}H_{33}N_5 \cdot 2HCl + 5H_2O$, crystallises in lustrous rhombic plates or prisms, which appear dark green by reflected light and deep red in transmitted light. No quinone dichlorodiimide is formed by the action of calcium hypochlorite.

Like the hexamethyl derivative, the octomethyl compound readily forms a leuco-base, and on reduction in hydrochloric acid solution is resolved into dimethylparatoluidine and paramidodimethylaniline, together with other substances which could not be isolated.

In all acridine derivatives hitherto prepared, the basic groups occupy the para-position relatively to the carbon atom which links the benzene nuclei, but in the preceding compounds the basic groups are in the meta-position relatively to the carbon atom, and in the para-position relatively to the nitrogen atom of the group $:C:N$; this probably accounts for the absence of fluorescence, and for the comparative instability of the compounds. The formation of the bases is explained by the assumption that part of the nitrosodimethylaniline is decomposed with the production of formic acid, whilst another portion combines with some of the dimethylaniline to form dimethylphenylene-green, $NMe_2 \cdot C_6H_4 \cdot N : C_6H_3 \cdot NMe_2$; the latter compound then condenses with the formic acid and the remaining dimethylaniline; hexamethyltetramidophenylacridine is therefore represented by the formula



and the octomethyl derivative by the formula



J. B. T.

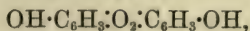
Xanthidrol. By R. MEYER and E. SAUL (*Ber.*, **26**, 1276—1279).

—*Xanthidrol*, $O < \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} > CH \cdot OH$, may be obtained by reducing xanthone in alcoholic soda solution with sodium amalgam. It forms tiny, colourless needles, does not melt at a definite temperature, and

with strong sulphuric acid, gives a yellow solution, with a green fluorescence. It is very readily oxidised to xanthone, which is formed when it is dried at rather over 100° , and also when attempts are made to condense it to diphenylenephnylmethane oxide. In one such attempt, however, when xanthidrol and benzene were heated with phosphoric anhydride, a small quantity of diphenylenemethane oxide, $O\langle C_6H_4 \rangle CH_2$, was formed. When xanthidrol is boiled with light

petroleum, it yields the ether $(O\langle C_6H_4 \rangle CH)_2O$ as nodular aggregates, also obtainable as short, lustrous crystals, which melt at about 200° . This substance is identical with that prepared by Richter (Abstr., 1884, 325), by reducing xanthone in alcoholic soda solution with sodium amalgam, and recrystallising the product from chloroform. He supposed it to be a compound of xanthone with diphenylenemethane oxide, but he really obtained xanthidrol in the first place, and unknowingly transformed it into its ether by crystallisation from chloroform. C. F. B.

Colouring Matters of the Triphenylmethane Series. By K. HOFMANN (*Ber.*, 26, 1139—1146).—By heating pyrogallol and benzaldehyde with zinc chloride, a brick-red substance is obtained, which has not the properties of an aurine dye; its constitution is perhaps represented by $O_2\langle C_6H_2(OH) \rangle CHPh$, a compound,

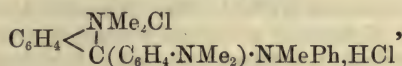


having been possibly formed as an intermediate product. With acetic anhydride and sodium acetate, this substance yields a brick-red diacetyl derivative; with a larger excess of anhydride and longer boiling, a reddish triacetyl derivative, $O_2\langle C_6H_2(OAc) \rangle CPhAc$?

When pyrogallol and benzaldehyde are heated with fuming hydrochloric acid at 100° in an open beaker, a red substance is obtained which has the properties of an aurine dye, and may be represented by the formula $O\langle CPh \text{ --- } C_6H_2(OH)_2 \rangle$. With acetic anhydride and

sodium acetate, it yields an orange-yellow triacetyl derivative which melts at 177° , and may be regarded as $O_2\langle C_6H_2(OAc) \rangle CPh \cdot OAc$. The formulæ suggested in the paper are, of course, tentative only. C. F. B.

Auramines. By A. STOCK (*J. pr. Chem.* [2], 47, 401—413).—Acetylphenylauramine zinc thiocyanate, $(C_{25}H_{28}N_3)CNS, Zn(CNS)_2 + 4H_2O$, was prepared by acetylising phenylauramine, treating the aqueous solution with potassium thiocyanate and zinc chloride, and salting out. It is a dark powder with a metallic lustre; acids and alkalis decompose it with formation of tetramethyldiamidobenzophenone, aniline, and acetic acid.

Methylphenylauramine hydrochloride,

obtained by heating methylaniline, tetramethyldiamidobenzophenone, and phosphorus oxychloride together in benzene, is a bright red, amorphous powder, and dissolves in chloroform, alcohol, and water; in the last two solvents it soon becomes decolorised, and, in the aqueous solution at all events, decomposed into methylaniline and tetramethyldiamidobenzophenone. The *zincochloride* was isolated. By passing dry ammonia into a chloroform solution of methylphenylauramine hydrochloride, methylaniline and auramine hydrochloride are produced.

Diphenylauramine results from the condensation of dimethylamidobenzodiphenylamide with dimethylaniline; its *zincochloride* was prepared.

Pentamethyleneauramine is obtained by the action of piperidine on tetramethyldiamidobenzophenone chloride. The *zincochloride* was prepared.

From this investigation, the author deduces the following generalisations concerning auramines: 1. They are derived from the triphenylmethane colouring matters by the substitution of an amido-group for one of the benzene nuclei. 2. Their colour depends on the basicity of the entering amido-residue; when this is strong, they are yellow, and as the basicity becomes more feeble, they pass into red; by the introduction of an acid residue, the colour becomes violet-blue. 3. The di-substituted auramines are decomposed by acids and alkalis into ketones and amines. 4. Dry ammonia eliminates the alkyl amido-residue as a secondary amine, and substitutes NH_2 for it. Aqueous ammonia behaves partly in this way and partly as an alkali (see above).
A. G. B.

Action of Phenylhydrazine on Lactones. By R. MEYER and E. SAUL (*Ber.*, 26, 1271—1276).—Phthalide, as W. Wislicenus found (*Abstr.*, 1887, 489), when heated with phenylhydrazine on the water-bath, yields an additive product, $\text{N}_2\text{H}_2\text{Ph} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OH}$. Diphenylphthalide and fluoran yield no compounds under these circumstances, but if boiled with phenylhydrazine they yield the condensation products, $\text{CO} \begin{array}{c} \text{C}_6\text{H}_4 - \\ \diagup \quad \diagdown \\ \text{N}_2\text{HPh} \end{array} \text{CPh}_2$ and $\text{CO} \begin{array}{c} \text{C}_6\text{H}_4 - \\ \diagup \quad \diagdown \\ \text{N}_2\text{HPh} \end{array} \text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{O}$ respectively. Phthalide itself yields no such derivative under these circumstances, but this is not surprising, since it decomposes at a temperature considerably below the boiling point of phenylhydrazine. The hydrazone of diphenylphthalide crystallises in colourless prisms melting at $230-231^\circ$, and, like diphenylphthalide itself, exhibits no fluorescence when dissolved in strong sulphuric acid. The hydrazone of fluoran crystallises in colourless needles melting, with partial decomposition, at $285-287^\circ$; like fluoran itself, it gives a fluorescent solution with strong sulphuric acid.
C. F. B.

Hydroximido-derivatives : Benzileoximes. By E. BECKMANN and A. KÖSTER (*Annalen*, 274, 1—36; compare Abstr., 1889, 1067).—The formation of benzoic acid and ammonia from α -benzilemonoxime has been already described (*loc. cit.*). Adopting the hypothesis of Hantzsch and Werner to explain the isomerism of the benzileoximes, the authors represent the α -monoxime by the formula

$\text{Ph} \cdot \overset{\text{N} \cdot \text{OH}}{\underset{\text{||}}{\text{C}}} \cdot \text{COPh}$; consequently the γ -monoxime must be represented by

the alternative formula $\text{Ph} \cdot \overset{\text{OH} \cdot \text{N}}{\underset{\text{||}}{\text{C}}} \cdot \text{COPh}$. These views, which it is urged

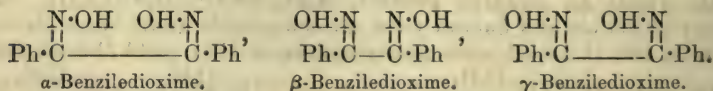
are justified by the results to be described, are in opposition to those of Hantzsch and Werner (Abstr., 1890, 350); compare also Claus (Abstr., 1892, 50).

When the α -monoxime is dissolved in ether and treated with phosphoric chloride, an oil, probably $\text{CPhCl} \cdot \text{N} \cdot \text{COPh}$, is obtained, which decomposes on distillation into a mixture of benzonitrile and benzoic chloride, and yields dibenzylazoxime on treatment with hydroxylamine. The α -monoxime decomposes when heated above 200° into benzonitrile and benzoic acid (see below).

On treating an ethereal solution of γ -benzilemonoxime with phosphoric chloride and subsequently shaking the product with an excess of soda solution, *benzoylformanilide*, $\text{NHPh} \cdot \text{CO} \cdot \text{COPh}$, is formed; it crystallises in golden-yellow needles, melts at 63° , and decomposes when heated with glacial acetic acid at 200° into benzoic acid, acetanilide, and formic acid.

It yields an *oximido*-compound, $\text{NHPh} \cdot \text{CO} \cdot \text{CPh} \cdot \text{NOH}$, which melts at 205 — 206° , is isomeric with the benziledioximes, and forms an *acetyl* derivative melting at 140° . Benzoylformanilide was also prepared by treating aniline benzoylformate with phosphoric chloride. When the γ -monoxime is heated with concentrated sulphuric acid, it yields benzoic acid, aniline, and sulphanilic acid, and when heated *per se*, it behaves in the same manner as the α -monoxime. Subsequent investigation proved, however, that when the α -monoxime is heated, it is converted into the γ -monoxime.

The authors ascribe the following formulæ to the benziledioximes.

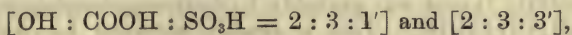


The α -dioxime yields the anhydrides, dibenzylazoxime, and isodibenzylazoxime (Abstr., 1889, 1067). The β -dioxime is converted into oxanilide by phosphoric chloride (*loc. cit.*), and when treated with sulphuric acid, oxanilideparasulphonic acid is formed. The γ -dioxime, on treatment with phosphoric chloride, yields phosphorus oxychloride, or sulphuric acid, dibenzylazoxime and benzoylphenylcarbamide, or their decomposition products. Under specific treatment, the γ -dioxime is converted into the α -dioxime, and under other circumstances, it is converted into the β -dioxime (compare Auwers and Meyer, Abstr., 1889, 713). Both the α - and the γ -dioximes

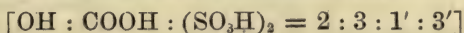
yield the normal anhydride of melting point 94° , but whilst an anhydride is only obtained from the γ -mouoxime by the hydrolysis of its acetyl derivative, the α -dioxime is converted into anhydrides under the circumstances mentioned above.

A. R. L.

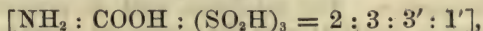
Constitution of β -Hydroxynaphthoic acid (m. p. 216°). By J. SCHMID (*Ber.*, **26**, 1114–1121).—This acid does not, as Hosaeus states (this vol., i, 355), yield a benzenetricarboxylic acid when oxidised with permanganate, nor does it, as he concludes, contain the hydroxyl and carboxyl groups in different rings. For a number of reasons, which it is impossible to reproduce here, the constitution of an orthohydroxynaphthoic acid is assigned to it, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{COOH}$ [$\text{OH}:\text{COOH} = 2:3$]. When oxidised with 10 per cent. alkaline permanganate on the water-bath, it yields nothing but phthalic acid. When sulphonated with concentrated sulphuric acid, it forms two isomeric β -hydroxysulphonaphthoic acids



of which the former yields well-crystallised normal salts, the latter well-crystallised acid salts, but very soluble normal salts which crystallise with difficulty. When these acids are fused with potash, they yield the corresponding *dihydroxynaphthoic acids* [$(\text{OH})_2:\text{COOH} = 2:1':3$] and [$2:3':3$], both crystallising in yellow needles, but melting, the former at $265\text{--}267^{\circ}$, the latter, with decomposition, at $225\text{--}228$. When either of the above-mentioned β -hydroxysulphonaphthoic acids, or β -hydroxynaphthoic acid itself, is heated at $100\text{--}140^{\circ}$ with fuming sulphuric acid (containing 24 per cent. SO_3), β -hydroxydisulphonaphthoic acid



is formed; this, when oxidised with permanganate, yields the same disulphophthalic acid as is obtained by the oxidation of the trisulphonic derivative of β -naphthol. When fused with soda, it yields *dihydroxysulphonaphthoic acid* [$(\text{OH})_2:\text{COOH}:\text{SO}_3\text{H} = 2:1':3:3'$], which forms pale yellow needles; the barium hydrogen salt crystallises from hot water with $2\text{H}_2\text{O}$. This acid is very stable towards soda; only when heated with potash at $310\text{--}320^{\circ}$, was an acid obtained, forming yellow needles melting at $255\text{--}257^{\circ}$ (? *trihydroxynaphthoic acid* [$(\text{OH})_3:\text{COOH} = 2:1':3':3$]). β -Hydroxydisulphonaphthoic acid, when heated at $240\text{--}280^{\circ}$ with strong aqueous ammonia, yields β -amidodisulphonaphthoic acid



forming white needles, and giving a yellowish-green fluorescence in alkaline solution. When this acid is heated with soda at $200\text{--}240^{\circ}$, it yields β -amidohydroxysulphonaphthoic acid [$\text{NH}_2:\text{COOH}:\text{SO}_3\text{H}:\text{OH} = 2:3:3':1'$], which crystallises in tufts of white prisms. When in this acid the NH_2 is displaced by OH by means of the diazo-reaction, the product is the dihydroxysulphonaphthoic acid described above.

C. F. B.

Constitution of β -Hydroxynaphthoic acid (m. p. 216°). By M. SCHÖPFF (*Ber.*, 26, 1121—1124).—As, contrary to Hosaeus' statement, β -hydroxynaphthoic acid (m. p. 216°) can be converted into a naphthacridine, it must be an *ortho*-hydroxynaphthoic acid. If β -anilidonaphthoic acid is heated with zinc chloride, phenonaphthacridone (melting at 242 — 244°) is formed, as already stated (Abstr., 1892, 1477), and this, when heated with zinc-dust in a current of hydrogen, yields a dihydrophenonaphthacridine melting at 167 — 168° . The acridone, when heated with dilute hydrochloric acid at 180° , is converted into an isomeride, melting above 290° , and insoluble in alkalis, $C_{10}H_{16} < \begin{smallmatrix} N \\ | \\ C(OH) \end{smallmatrix} > C_6H_4(?)$; this substance is obtained from β -anilidonaphthoic acid directly by heating it with dilute hydrochloric acid at 180° , and also from β -hydroxynaphthoic anilide by heating it with zinc chloride at 230 — 250° .

The substance mistaken by Hosaeus for benzenetricarboxylic ("hemimellitic") acid was probably 1 : 2-carboxyphenylglyoxylic acid, $COOH \cdot C_6H_4 \cdot CO \cdot COOH$. This is readily obtained by oxidising β -hydroxynaphthoic acid with alkaline permanganate at the ordinary temperature. The acid itself, obtained by extraction with ether, forms an oil which gradually solidifies to a mass of needles. By warming the solution with phenylhydrazine hydrochloride at 80° , phenylphthalazonecarboxylic acid, $CO < \begin{smallmatrix} C_6H_4 \\ N_2Ph \end{smallmatrix} > C \cdot COOH$, is obtained, forming colourless needles melting at 221 — 222° , and doubtless identical with the substance melting at 214 — 215° obtained by Henriques from a compound formed by oxidising β -naphthol with alkaline permanganate at the ordinary temperature (Abstr., 1888, 842).

C. F. B.

β -Hydroxynaphthoic acid (m. p. 216°). By R. HIRSCH (*Ber.*, 26, 1176—1179; compare Hosaeus, this vol., i, 355; Schmid and Schöpf, preceding abstracts).— β -Hydroxynaphthoic acid (1 part) is treated with sulphuric acid (2 parts) at 75° , the product is converted into the calcium salt, and, on evaporation, crystals (A) are deposited; the mother liquor, on concentration, yields a second pulverulent salt (B), which is separated from the hot solution; on further evaporation, the filtrate deposits crystals of the compound A.

The salt A is soluble in about 14 parts of water at 100° , and crystallises with $5H_2O$; the potassium salt is deposited from alcohol in prismatic aggregates, and becomes yellow when heated, but on cooling the colour disappears. The sulphonie acid is prepared from the calcium salt, and is identical with the compound prepared by Hosaeus (*loc. cit.*); it gives a violet-blue coloration with ferric chloride, and forms a dye with diazo-compounds.

The salt B dissolves in about 75 parts of water at 100° ; the barium salt is sparingly soluble; the potassium, sodium, and ammonium salts readily dissolve, and the solutions are slightly fluorescent; they give a violet-blue coloration with ferric chloride, and undergo scarcely any alteration on heating. The sulphonie acid

is more sparingly soluble than the isomeric compound, and does not combine so readily with diazo-compounds.

The author considers that the properties of the above compounds prove that in β -hydroxynaphthoic acid the groups occupy the positions 2 : 3; there is no proof that Hosaeus' sulphonic acid is not an ortho-compound, since the hydroxyl would probably exert quite as much influence as the carboxyl on the position of the sulphonic group, but, apart from this, the acid is as likely to be a dis-heteronuclear compound as it is to be a meta- or para-homonuclear compound.

J. B. T.

1 : 1'-Naphthalic acid and its Derivatives. By G. F. JAUBERT *Chem. Centr.*, 1893, i, 572—573; from *Arch. sci. phys. nat. Genève*, 29, 141—161).—1 : 1'-Naphthalic acid is prepared by oxidising acenaphthene dissolved in glacial acetic acid (6 parts) with potassium dichromate (12 parts). The oxidation product is precipitated with acid, the precipitate treated with 5 per cent. soda solution, which dissolves the naphthalic acid from the bye-products, and it is finally crystallised from nitric acid (sp. gr. 1.48), from which a portion of the acid separates as anhydride; the remainder of the acid is precipitated by the addition of water. It is converted into the *anhydride*, $C_{10}H_6<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>O$, when heated at 180° ; the latter forms white needles, melts at 274° , and is almost insoluble in water, very sparingly soluble in ether, and only slightly so in alcohol. It is not attacked by chlorine, phosphoric chloride, or sulphur dichloride.

The *imide*, $C_{10}H_6<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>NH$, is formed on treating the anhydride with ammonia; it melts at 300° , and may be crystallised from cold concentrated nitric acid.

The *sodium* and *potassium* derivatives were prepared; the *methyl* derivative, $C_{10}H_6<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>NMe$, melts at 205° ; the *ethyl* derivative melts at 148° , the *phenyl* derivative at 202° , the *benzyl* derivative at 196.6° , and the *orthotolyl* derivative at 214.2° .

When 1 : 1'-naphthalic anhydride is treated with hydroxylamine, it yields a colourless *oxime*, $C_{10}H_6<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>NOH$, melting at 284° ; its *metallic* derivatives are red, brown, or yellow; the *methyl* derivative melts at 211° , and the *ethyl* derivative melts at 160° . An analogue of anthranilic acid is not formed by treating the sodium derivative of the oxime with alcoholic soda.

The *phenylhydrazone*, $C_{10}H_6<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>N_2HPh$, melting at 218.5° , is obtained by treating 1 : 1'-naphthalic anhydride with phenylhydrazine; the *acetyl* derivative melts at 230° , and the *benzoyl* derivative at 230.5° . On reduction with zinc or tin and hydrochloric acid, the hydrazone furnishes hydroxynaphthalide (*Abstr.*, 1892, 864), but experiment failed to produce a compound analogous to phthalide by the reduction of the above-mentioned naphthalimide.

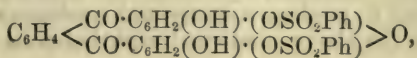
A. R. L.

Amidonaphtholsulphonic acids. By F. REVERDIN and C. DE LA HARPE (*Ber.*, 26, 1279—1284; compare Abstr., 1892, 996).—An *amidonaphtholsulphonic acid* [$\text{OH} : \text{NH}_2 : \text{SO}_3\text{H} = 1 : 2 : 4$ or $1 : 2 : 4'$] is obtained by the direct sulphonation of 1:2-amidonaphthol, which is itself got by reducing 1:2-nitrosonaphthol (best obtained from 1:2-hydroxynaphthoic acid and nitrous acid) with stannous chloride. It oxidises on standing in sodium carbonate solution to a violet-black dye, and has all the properties of the 1:2:4-acid previously described (Abstr., 1892, 996), but may possibly have the 1:2:4'-constitution. An isomeric acid [$\text{OH} : \text{NH}_2 : \text{SO}_3\text{H} = 1 : 4 : 3$] is obtained by reduction of the nitroso-derivative of 1:3-naphtholsulphonic acid or of the azo-dye which this acid yields with diazobenzene chloride. It yields a small quantity of a greenish-brown colouring matter when oxidised.

Amidonaphtholdisulphonic acid [$\text{OH} : \text{NH}_2 : (\text{SO}_3\text{H})_2 = 1 : 2 : 4 : 3'$] is obtained from 1:4:3'-naphthylaminedisulphonic acid by converting it, by means of the diazo-reaction, into naphtholdisulphonic acid, combining this with diazobenzene chloride, and reducing the product. By the addition of sodium chloride, it can be separated from solution in white needles, probably as the sodium hydrogen salt. When oxidised, it yields a violet-black dye. The isomeric 1:2:4:2'-acid is obtained in a similar manner from 1:4:2'-naphthylaminedisulphonic acid; also by reducing the nitroso-derivative of 1:4:2'-naphtholdisulphonic or the compound of diazobenzene chloride with 1:2:4:2'-hydroxydisulphonaphthoic acid; it forms white needles, and, when oxidised, yields a dirty red dye. A third isomeric 1:2:4:1'-acid is obtained by reducing the compound of diazobenzene chloride with the 1:4:1'-naphtholdisulphonic acid obtained by sulphonating naphthosulphone. It is a well-crystallised substance, and, when oxidised, yields a greenish-black dye. All these disulphonic acids can be diazotised, and the products yield dyes with resorcinol, β -naphthol, and β -hydroxynaphthoic acid, in the last case of a bluish-violet colour. 1:4:2:7-Amidonaphtholdisulphonic acid and the 1:2:4-monosulphonic acid can be only partially diazotised.

Amidonaphtholsulphonic acid [$\text{OH} : \text{NH}_2 : \text{SO}_3\text{H} = 2 : 1 : 4'$], from 2:4'-naphthylaminesulphonic acid, has been shown to be identical with that previously obtained from the naphthylaminesulphonic acid γ - of the Badische Anilin und Soda Fabrik. C. F. B.

Some Benzenesulphonates of the Aromatic Series. By M. GEORGESCU (*Chem. Centr.*, 1893, i, 302; from *Bull. Soc. Sci. Fiz. Bucuresti*, 1892, 213; compare Abstr., 1891, 49, 202, and 568).—Benzenesulphonic chloride reacts with alizarin, anthrapurpurin, and gallein, forming the following compounds:—*Alizarin benzenesulphonate*, $\text{C}_6\text{H}_4 : \text{C}_2\text{O}_2 : \text{C}_6\text{H}_2(\text{O} \cdot \text{SO}_2\text{Ph})_2$, melting at 182 — 184° ; *anthrapurpurin benzenesulphonate*, $\text{C}_8\text{H}_5 \cdot \text{SO}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_3 : \text{C}_2\text{O}_2 : \text{C}_6\text{H}_2(\text{OPh})_2$ (?), melting at 182 — 186° ; *gallein dibenzenesulphonate*,



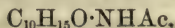
which appears to decompose at 100—120°; and *gallein tetrahenzenesulphonate*, $C_6H_4 \left\langle \begin{smallmatrix} CO \cdot C_6H_2(O \cdot SO_2Ph)_2 \\ CO \cdot C_6H_2(O \cdot SO_2Ph)_2 \end{smallmatrix} \right\rangle O$, melting at 187—188°.

A. R. L.

Isonitrosocamphor and its Derivatives. By L. CLAISEN and O. MANASSE (*Annalen*, 274, 71—94).—A better method for the preparation of isonitrosocamphor than that previously given (Abstr., 1889, 619) is described. Sodium in the form of wire is added to an ethereal solution of camphor, and the mixture poured into amyl nitrite cooled by ice; the resulting sodium salt is dissolved in water and decomposed by acetic acid. Isonitrosocamphor crystallises in rhombic prisms, $a : b : c = 0.8775 : 1 : 0.6361$; it is much more stable than Cazeneuve's nitrosocamphor (Abstr., 1889, 720). The *phenylhydrazone*, $C_8H_{14} \left\langle \begin{smallmatrix} C \cdot NOH \\ C \cdot N_2HPh \end{smallmatrix} \right\rangle$, forms small, yellow needles, melts at 130°, and has acidic properties; it dissolves in concentrated sulphuric acid with a deep purple colour which changes to blue on the addition of sodium nitrite, and an alcoholic solution gives a dark red coloration on addition of ferric chloride. When isonitrosocamphor is gently heated with fuming hydrochloric acid, it dissolves with ebullition, and camphoramic acid, $NH_2 \cdot CO \cdot C_8H_{14} \cdot COOH$, is obtained. This crystallises from boiling water in colourless leaflets, melts at 174—176°, and when heated above its melting point yields camphoric anhydride (not camphoric imide, as stated by Laurent, *Annalen*, 60, 326). When isonitrosocamphor is heated for some hours on the water-bath with fuming hydrochloric acid, camphoric acid and camphoric imide, $C_8H_{14} \left\langle \begin{smallmatrix} CO \\ CO \end{smallmatrix} \right\rangle NH$, melting at 244—245° (corr.), are formed (compare Abstr., 1890, 1152).

The preparation and properties of camphororthoquinone have been already described (Abstr., 1889, 619). The yellow solution of the quinone is not decolorised by sulphurous acid, but when the compound is boiled with aqueous alkalis camphoric acid is formed. The *phenylhydrazone*, $C_8H_{14} \left\langle \begin{smallmatrix} C \cdot N_2HPh(\beta) \\ CO(\alpha) \end{smallmatrix} \right\rangle$, crystallises in yellowish prisms, and melts at 170—171°; it is identical with the compound obtained by Claisen and Bishop (*Sitzungsber. kgl. Bayer. Akad.*, 1890, 460 and 478) by the action of diazobenzene chloride on hydroxymethylenecamphor.

Amidocamphor, $C_{10}H_{15}O \cdot NH_2$, is obtained by reducing isonitrosocamphor with zinc-dust and acetic acid; it boils at 243—245°, and is probably identical with the compound obtained by Schiff (Abstr., 1880, 891; compare also Kachler and Spitzer, *Monatsh.*, 4, 567). The *hydrochloride* crystallises in needles, and melts at 223—225°; the *platinochloride* and *nitrite* are crystalline. The *formyl* derivative, $C_{10}H_{15}O \cdot NH \cdot CHO$, melts at 76—77°; the *acetyl* derivative,



melts at 108°, and the *benzoyl* derivative melts at 140°. A. R. L.

Champacol, a New Camphor. By E. MERCK (*Arch. Pharm.*, 231, 123).—*Champacol*, $C_{17}H_{30}O$, occurs in champaca-wood, and is obtained from it by steam distillation. It crystallises in long, white, matted needles, has no odour, melts at $86-88^{\circ}$, and can be sublimed. When pure, it is stable, but when impure, it liquefies, and a smell of champaca-wood can be perceived. C. F. B.

Hydroxymethylene Compounds. By L. CLAISEN (*Ber.*, 26, 1173).—The statement attributed to v. Pechmann (this vol., i, 360), that the methyl derivative of oxymethylenecamphor is an oil, was due to a misapprehension on the part of the author. C. F. B.

Gum Benzoïn from Sumatra. By F. LÜDY (*Arch. Pharm.*, 231, 43—95).—This substance, which differs from that obtained from Siam, has been very carefully examined. Contrary to previous statements, it is entirely soluble in ether, fragments of wood, of course, excepted. The α -, β -, and γ -resins of earlier investigators are shown to be mixtures of partially hydrolysed cinnamates of benzoiresorcinol and resinotannol, the α -resin being the least and the γ - the most hydrolysed; the α - and β -resins can, by boiling with caustic potash, be converted into the γ -resin, which is thus the sole product of the prolonged action of caustic potash on the resin of gum benzoïn. No resin is contained in the uninjured bark; it is formed as a consequence of the injury.

The author summarises his results as follows:—Gum benzoïn (from Sumatra) is soluble in ether, and the dissolved substance yields 0.01 per cent. ash. It contains, besides benzoic acid and cinnamene, (1) benzaldehyde, traces; (2) benzene, traces; (3) vanillin, 1 per cent.; (4) phenylpropylic cinnamate, 1 per cent.; (5) cinnamyl cinnamate, 2—3 per cent.; (6) a mixture of a little *benzoiresinol cinnamate* with much *resinotannol cinnamate*, this mixture forming the main constituent of the gum. In addition to these, woody impurities are present to the extent of 14—17 per cent. Free cinnamic acid occurs in gum benzoïn, although to a less extent than free benzoic acid; by far the greater part of it, however, exists in combination. By hydrolysis of the mixture of benzoiresinol and resinotannol cinnamates, there are obtained cinnamic acid and two alcohols—the white, crystallised *benzoiresinol*, $C_{16}H_{26}O_2$, and the brown, amorphous *resinotannol*, $C_{18}H_{20}O_4$. From benzoiresinol there were obtained a *potassium derivative*, and *methyl*, *ethyl*, and *isobutyl* (mono-) *derivatives*; these all crystallise in white needles. Benzoiresinol itself yields, with strong nitric acid an amorphous oxidation product containing nitrogen; no acetic or benzoic derivative could be obtained from it, and no oxime; with bromine, it yields an amorphous bromo-derivative. From resinotannol were obtained a *potassium salt* and a *monethyl derivative*, both as brown, amorphous substances. Resinotannol itself is oxidised by strong nitric acid to picric acid; dilute nitric acid forms a nitro-derivative, and an oxidation product of the nature of a phlobaphen; bromine forms amorphous bromo-derivatives very rich in bromine. When reduced, it yields a white substance which oxidises so readily that it could not be further investigated. When

fused with caustic potash, it yields butyric acid, phenol, and proto-catechuic acid.

The bark of uninjured trees of *Styrax Benzoin Dryand* contains, besides traces of wax and a little phloroglucinol and sugar, large quantities of a tannin which very readily oxidises to a phlobaphen, *benzophlobaphen*, $C_{51}H_{50}O_{21}$, a lustrous, reddish-black powder.

Since the uninjured bark contains neither secreting vessels nor secretions, but, on the other hand, does contain a large quantity of tannin, particularly in the medullary rays, and since gum benzoin contains large quantities of an alcohol, resinetannol, which has the characters of a tannin, and since, finally, the formation of resin begins in the medullary rays, therefore it is probable that the gum is formed from the tannin of the bark, increases in amount by a process of backward metamorphosis of the cell-membranes, and is then stored up in lysigenetic spaces; if these spaces increase largely in bulk, they form resin glands. C. F. B.

Constituents of Sumatra Gum Benzoin. By E. SCHMIDT (*Arch. Pharm.*, **231**, 95—98).—A large quantity of genuine gum benzoin from Sumatra was examined some time ago by C. Denner, a former demonstrator in the author's laboratory: the results were, however, never published, owing to the death of Denner, and loss of his MSS. His results confirmed, to a large extent, those of Lüdy (preceding abstract), and he was able to demonstrate more satisfactorily than the latter the existence of benzaldehyde and cinnamene in the gum. C. F. B.

Adonite. By E. MERCK (*Arch. Pharm.*, **231**, 129—131).—Adonite, $C_5H_{12}O_5$, is contained to the extent of 4 per cent. in the flowering shoots of *Adonis vernalis*. It crystallises from water in long, colourless prisms, from alcohol in short, white needles, melts at 102° , and decomposes when distilled, is a neutral substance, and does not reduce Fehling's solution; possibly it is a pentahydric alcohol. It is without specific physiological action. C. F. B.

Cerberin. By P. C. PLUGGE (*Arch. Pharm.*, **231**, 10—34).—This substance discovered by De Vrij, occurs in the seeds of an Indian tree, *Cerbera odollam*, Gaertn. (*C. mangas*, L.; *Tanghinia odollam*, Don.). It forms colourless, odourless crystals with a bitter taste, turns yellow at 180 — 185° , and melts at 191 — 192° (corr.). It dissolves in the following substances, 1 part in the indicated number of parts of the solvent at 16 — 21° :—Chloroform, 8.83; alcohol, 90 per cent., 12.43, absolute, 12.89, 75 per cent., 27.27; isobutyl alcohol, 14.7; amyl alcohol, 14.87; ether, 178.5; benzene, 544.7; carbon tetrachloride, 813; water, 5555 (at 100° , 4974); carbon bisulphide, 12,487; light petroleum (sp. gr. 0.675), 36,730. It has the following values of specific rotation, $[\alpha]_D$; in 90 per cent. alcohol, -74.61° ; in ether, -64.76° ; in chloroform, -74.82° ; in acetic acid, -80.81° . Analysis and molecular weight determinations lead to the formula $C_{27}H_{40}O_8$; but its properties show that it is not identical either with the tanghinin of Arnaud or with the thevetin of De Vrij. It exhibits

the following colour reactions:—I. Yellow coloration when warmed with dilute sulphuric, hydrochloric, or nitric acid. II. Polychroic solution (orange-yellow-violet-blue) in concentrated sulphuric acid. III. A quickening, emphasising, and sometimes a characteristic modifying, of colour reaction II, when to the sulphuric acid are added small quantities of (a) phenols (thymol, α -naphthol, cresol, or glycolcholic acid), or (b) aldehydes (furfuraldehyde, cane sugar, vanillin, heliotropin, &c.). Reaction III (a) seems to indicate that cerberin is a glucoside, III (b) that it is a phenol. As a matter of fact, cerberin is hydrolysed when heated with alcoholic sulphuric acid for two hours, and yields a small quantity of sugar, probably glucose, and 62 per cent. of *cerberetin* $C_{19}H_{26}O_4$ (?), a lemon-yellow, amorphous powder, which melts at 85.5° (corr.), is optically inactive, and is precipitated from its solution in alcohol by the addition of water; the alcoholic solution has, even when diluted to 1:5000, a perceptible yellow colour. Like cerberin, it is a poison. Observations of the physiological action of cerberin agree with those of Zotos (Dissertation, Dorpat, 1892); it has the advantages, without the disadvantages, of digitalin.

C. F. B.

Glucoside of *Ipomœa pandurata* (*Convolvulus panduratus*, L.). By N. KROMER (*Chem. Centr.*, 1893, i, 427—428; from *Pharm. Zeit. Russ.*, 32, 1—5, 17—21, 33—38).—The drug *Ipomœa pandurata*, Meyer (man in the ground root, man root, man of the earth, wild jalap, and wild potato), is used in America as a remedy for lithiasis. The root is cylindrical, 2—3 feet in length and 1 or more inches in thickness; it diminishes in thickness suddenly to the size of a finger, and exudes a milky, resinous juice. Its exterior is greyish-brown and its interior greyish-white; it has a characteristic bitter taste.

In order to obtain the glucoside described by Manz (1881), the author employed the method used for extracting the glucosides from other *Convolvulaceæ* (*Chem. Centr.*, 1893, i, 310), and found that the chief constituent of the root was a compound *ipomœin*, $C_{78}H_{132}O_{36}$, together with a small quantity of a semi-fluid compound. *Ipomœin* is a white powder, melting at 170° , soluble in most solvents except ether, gives a red coloration with sulphuric acid and an intense red coloration with sodium hydroxide. By the action of barium hydroxide, a volatile acid, $C_5H_8O_2$ (probably β -methylecrotonic acid) is formed together with *ipomœic acid*, $C_{34}H_{62}O_{18}$, which is a bright-yellow amorphous powder; it softens at 115° and melts at 135 — 140° . Mineral acids convert the last-named acid into *ipomeolic acid*, a monobasic acid crystallising in concentrically grouped needles, and melting at 60.6° , and a cupric reducing sugar giving a *phenylhydrazine compound* (?) melting at 198° .

Ipomœin is decomposed by mineral acids into ipomeolic acid, a sugar, and a volatile acid, $C_6H_8O_2$, (m. p., 60.8°), which is perhaps β -methylecrotonic acid. Nitric acid converts ipomœin into a sebacic acid, $C_{10}H_{18}O_4$, which crystallises in needles, is soluble in hot water, and melts at 98.6° , together with a valeric acid.

A. R. L.

Derivatives of Cantharidin. By F. ANDERLINI (*Gazzetta*, 23, i, 121—128).—Cantharidin dissolved in absolute alcohol is reduced by sodium; after treating the product with water, distilling off the alcohol, and acidifying, the unchanged cantharidin is deposited and may be separated. By extracting with ether, evaporating, dissolving the residue in benzene, and fractionally precipitating by petroleum, a colourless, crystalline *substance* is finally obtained; this has the composition, $C_{10}H_{14}O_3$, melts at 129° , and is very soluble in alcohol or benzene, but less so in water.

Cantharidin hydrazone dissolves in nitric acid yielding a bright yellow *dinitro-derivative*, $C_{16}H_{16}(NO_2)_2NO_3$, which does not melt at 320° ; it dissolves in glacial acetic acid, but is insoluble in most other solvents. With alkalis, it gives a scarlet colour; on reduction with zinc dust and acetic acid, a red or yellow solution is obtained, from which the substance melting at 201° previously described by the author (Abstr., 1890, 640) may be isolated. Nothing but negative results were obtained on reducing the nitrohydrazone with sodium in alcoholic solution.

On boiling cantharidinimide with phosphorus oxychloride, a *substance* of the composition $C_{10}H_{11}NO_2$ is produced; it forms monosymmetric prisms, $a:b:c = 2.001:1:2$; $\beta = 65^\circ 28'$, melting at 137° .

W. J. P.

Action of Diamines on Cantharidin. By F. ANDERLINI (*Gazzetta*, 23, i, 128—139).—On mixing an alcoholic solution of ethylenediamine with finely divided cantharidin, heat is developed, and a white additive *compound*, $C_{10}H_{13}O_4, C_2H_4(NH_2)_2$, is formed; it melts at 195° with decomposition, is very soluble in water, but insoluble in alcohol, ether, or benzene, and gives cantharidin when boiled with hydrochloric acid. A *compound* of the composition $C_{11}H_{14}O_3N$ is obtained on heating the mixture of alcohol, ethylenediamine, and cantharidin in a closed tube at 100° ; it forms colourless, flattened, monosymmetric prisms of pearly lustre, $a:b:c = 2.2811:1:1.7906$; $\beta = 75^\circ 58'$. It melts at 219 — 220° and is soluble in most of the ordinary solvents. It is a neutral substance, and is not attacked by long heating with potash or baryta. After separating this compound, a *base* of the composition $C_{12}H_{18}O_3N_2$ is found in the mother liquors. It is a white crystalline substance which melts at 94 — 95° , when deposited from its syrupy aqueous solution; it separates from ether in transparent crystals which melt at 50 — 53° owing to their containing ether of crystallisation; this is lost on exposure to air. The *hydrochloride* is employed in the purification of the base; it forms colourless, transparent, anorthic plates, $a:b:c = 1.2639:1:0.5515$; $\alpha = 75^\circ 27'$, $\beta = 78^\circ 42'$, $\gamma = 90^\circ 55'$; it is very soluble in water, but only sparingly so in alcohol. The *platinochloride* is obtained in brilliant-yellow prisms or laminae and turns brown at 250° ; it is soluble in water.

On heating cantharidin and orthophenylenediamine in glacial acetic acid solution in a reflux apparatus, condensation occurs with elimination of $2H_2O$ and a white, crystalline *substance* is obtained, which has the composition $C_{16}H_{16}O_2N_2$, and melts at 163° . It is neutral towards in-

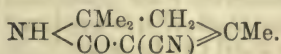
dicators, and insoluble in dilute acids, but dissolves in the ordinary solvents, with the exception of water.

Orthotoluylenediamine reacts in the same way with cantharidin, yielding a crystalline *substance* of the composition $C_{17}H_{17}O_2N_2$, which melts at $180-181^\circ$ and is similar in properties to the preceding compound.

W. J. P.

New Method of synthesising Hydropyridine Compounds.

By J. GUARESCHI (*Chem. Centr.*, 1893, i, 699—700; from *Ann. Chim. Farm.*, 17, 83—87).—The method consists in the action of ethylic cyanacetate on acetone or other ketones in the presence of ammonia; or in other words, the action of ethylic cyanacetate on diacetonamine, which latter is formed during the reaction. When an ethereal solution of the ready-formed diacetonamine is treated with ethylic cyanacetate, a white compound melting at $194-195.5^\circ$ is obtained; it is also formed by treating acetone or mesityl oxide, saturated with dry ammonia, with ethylic cyanacetate. The author believes this compound to be *cyanotrimethyldihydro-2-pyridone*,



Similar compounds are formed when instead of ammonia a primary amine is used. The compound $C_{10}H_{14}N_2O$, obtained from acetone, methylamine, and ethylic cyanacetate, melts at $142-143.5^\circ$, and is more sparingly soluble in potash than the lower homologue. On oxidation with permanganate, two crystalline compounds are obtained; one is an *amide*, and the other an acid melting at $172-174^\circ$; the latter gives a blood-red coloration with ferric chloride. The corresponding *benzyl* derivative, $C_{16}H_{18}N_2O$, melts at $168-169^\circ$; and the *allyl* derivative, $C_{12}H_{16}N_2O$, melts at $152-153.5^\circ$.

A. R. L.

4'-Bromonicotinic Acid. By A. CLAUS and E. PYCHLAU (*J. pr. Chem.* [2], 47, 414—420).—4'-Bromonicotinic acid (Abstr., 1892, 876) forms tabular or columnar, vitreous crystals, with $2H_2O$; it melts at 183° , and sublimes without decomposition. The *ammonium* salt, $C_5NH_3Br \cdot COONH_4$, the *sodium* salt with $1H_2O$, the *potassium* salt with $1\frac{1}{2}H_2O$, the *calcium* salt with $2H_2O$, the *barium* salt with $4H_2O$, the *silver* salt, the *cobalt* salt with $1H_2O$, the *nickel* salt with $2H_2O$, and the *copper* salt are described.

The acid previously described as 3'-bromonicotinic acid (*loc. cit.*), is now shown to be *nicotinic acid hydrobromide*, $C_5NH_4 \cdot COOH \cdot HBr$, and is remarkable for the constancy of its melting point (275°), and for its subliming unchanged.

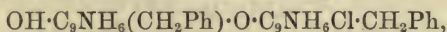
4'-Bromonicotinic acid hydrobromide crystallises from a solution of the acid in hydrobromic acid in aggregates of needles, melts at 243° , and sublimes unchanged.

A. G. B.

Hydroxyquinolines. By A. CLAUS and H. HOWITZ (*J. pr. Chem.* [2], 47, 426—438; compare Abstr., 1892, 878).—1-Hydroxyquinoline 1'-ethobromide crystallises in hard, yellow prisms with $2\frac{1}{2}$ mols. H_2O ,

and when dried at 100° melts at 166° . The "*intermediate product*," $\text{OH}\cdot\text{C}_9\text{NH}_6\text{Et}\cdot\text{O}\cdot\text{C}_9\text{NH}_6\text{EtBr}$, obtained by decomposing the ethobromide in aqueous solution with half a molecular proportion of an alkali hydroxide, crystallises in slender, scarlet needles, and when quickly heated, melts at 177° (compare Abstr., 1892, 878). This product is also formed when an excess of alkali is used if the solution be dilute and cold, otherwise 1-hydroxyquinoline-1'-ethoxide is produced; this crystallises in large, brilliant, dark-red tables or columns with $1\text{H}_2\text{O}$, and dissolves easily in alcohol, but not at all in absolute ether; it melts in its water of crystallisation at 72° , and, when anhydrous, softens at 220° , but decomposes before fusion.

The 1'-benzochloride, $\text{OH}\cdot\text{C}_9\text{NH}_6\text{Cl}\cdot\text{CH}_2\text{Ph}$, is prepared by heating its components at 130 — 135° in a sealed tube for 18—20 hours; it forms small, golden-coloured crystals with $1\text{H}_2\text{O}$, melts in its water of crystallisation at 75° , and when anhydrous at 182° , and dissolves in hot water. The "*intermediate product*,"



crystallises in slender, orange-red needles with $1\text{H}_2\text{O}$, melts with decomposition at about 145° , and dissolves easily in water. The benzohydroxide crystallises in large, brilliant, dark-red prisms and columns with $1\text{H}_2\text{O}$; it melts in its water of crystallisation at 66° , and when anhydrous between 140° and 150° ; it dissolves in water, but not in ether.

It has been previously stated (*loc. cit.*) that a quaternary ammonium hydroxide, sufficiently stable not to become converted into a base soluble in ether, is only produced from a hydroxyquinoline alkyl haloid when the hydroxyl group has the 2- or 3-position in the benzene ring. The obtaining such compounds from 1-hydroxyquinoline derivatives, as described above, refutes the statement in question, which must therefore be withdrawn.

4-Hydroxyquinoline has been obtained by the usual reactions from quinoline-4-sulphonic acid, and from 4-amidoquinoline; it is a pale-yellow, crystalline powder, which melts with decomposition at 224° . The hydrochloride forms small, yellow crystals, and melts at 240° . The platinochloride, with $4\text{H}_2\text{O}$, is described. The methiodide crystallises both in short, brownish-red, lustrous columns, and in thin, golden-yellow aggregates of ill-defined form; both melt at 224° , and dissolve somewhat easily in water, separating therefrom as a viscid oil, which slowly solidifies. The methohydroxide crystallises in brilliant, dark-red, vitreous columns, and dissolves in water and alcohol, but not in ether.

A recantation is also necessary with regard to the action of potassium hydroxide on 4-hydroxy-3-chloroquinoline methiodide (*loc. cit.*). The authors have since found that their ether contained alcohol, which dissolved the base produced, and that when pure ether is used nothing is dissolved, so that in this case also the methoxide formed is insoluble in ether.

Further investigations are being conducted on the bases derived from the alkyl haloids derived from the hydroxyisoquinolines (compare *loc. cit.*).

A. G. B.

Pyrazines and Piperazines. By C. STOEHR (*J. pr. Chem.* [2], 47, 439—522).—The author has prepared pyrazine by distilling piperazine, or its hydrochloride, with zinc-dust, the yield being about 10 per cent. Obtained in this way, it is a limpid, mobile, highly refractive liquid, which boils at 138—140° (corr.); it volatilises easily with steam, and has a penetrating odour resembling that of the pyridine bases; it dissolves easily in water, alcohol, and ether, and is separated from its aqueous solution by caustic alkalis; its sp. gr. at 0°/4° is 1.0317; it is a feebler base than its homologues, and has not yet been crystallised (compare Wolff, this vol., i, 373). The hydrochloride is easily dissociated. The picrate forms yellow needles. The *mercury chloride* compound, $C_4H_4N_2 \cdot HgCl_2$, is very sparingly soluble, and forms lustrous crystals. The aurochloride, $C_4H_4N_2 \cdot HAuCl_4$, crystallises in lustrous, yellow laminae, and melts with decomposition at 245° (compare Wolff, *loc. cit.*).

2 : 5-Dimethylpyrazine, $N \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{CH} : \text{CMe} \end{smallmatrix} N$, has been already described as dimethyldiazine (Abstr., 1891, 581; 1892, 507). Besides the platinochlorides previously described (Abstr., 1891, 581), the *salt* $(C_6H_5N_2)_2 \cdot H_2PtCl_6 + 4H_2O$ has been obtained. The aurochloride crystallises with $1H_2O$, not $\frac{1}{2}$ mol., as previously stated (*loc. cit.*), and, when anhydrous, melts at 153°. The *mercury chloride* compounds, $C_6H_5N_2 \cdot 2HgCl_2$, and $C_6H_5N_2 \cdot 3HgCl_2$, are described, and a third one, containing even more mercuric chloride, was crystallised, but not analysed. The solutions of the base are also precipitated by zinc chloride and silver nitrate. The *picrate*, $C_6H_5N_2 \cdot C_6H_2(NO_2)_3 \cdot OH$, crystallises in laminae, prisms, and needles, and melts at 157° (compare Abstr., 1892, 507).

Ketine, another dimethylpyrazine, was studied by Treadwell and Steiger (Abstr., 1882, 941). It is best prepared by reducing isonitrosoacetone with zinc and hydrochloric or acetic acid. It is a colourless, highly refractive liquid, which boils without decomposition at 155° (760 mm., mercury column in vapour), and resembles 2 : 5-dimethylpyrazine in odour; indeed there is reason to believe that these two bases are identical. Ketine dissolves in water with alkaline reaction, and separates again on the addition of caustic alkali. Its sp. gr. at 18°/4° is 0.9896; when quickly cooled, it crystallises in rhombohedra, which melt above 15°. The platinochlorides are quite similar to those of 2 : 5-dimethylpyrazine (see above), and the resemblance obtains with all the other salts which are described.

2 : 5-Dimethyl-3-ethylpyrazine, $N \begin{smallmatrix} \text{CMe} \cdot \text{CEt} \\ \text{CH} : \text{CMe} \end{smallmatrix} N$, has been already described (Abstr., 1891, 582). Its constitution is settled by the fact that its oxidation product, $C_7H_9N_2O_2$, yields 2 : 5-dimethylpyrazine by loss of carbonic anhydride. The *platinochlorides*, $C_8H_{12}N_2 \cdot H_2PtCl_6 + 2H_2O$; $C_8H_{12}N_2 \cdot HCl$, $PtCl_4$; and $C_8H_{12}N_2 \cdot PtCl_4$, are described. The *mercurochloride*, *argentonitrate*, and *zincchloride* were obtained. The *picrate* crystallises in long, yellow needles, and melts at 142°. The *methiodide* crystallises in laminae and needles, and melts with decomposition at 236—237°.

Pyrazinecarboxylic acid, the ultimate product of the oxidation of dimethylethylpyrazine with potassium permanganate, crystallises in needles (with $1\frac{1}{2}$ mols. H_2O), melts, with decomposition, at 177° , and partially sublimes; it dissolves in hot water, alcohol, ether, hot benzene, and hot chloroform; with ferrous chloride, it gives a violet-red colour. A *platinochloride* can be obtained in a strong hydrochloric acid solution of the acid. The *ammonium*, *barium*, *calcium*, *tin*, *lead*, *silver*, *copper*, *cobalt*, *nickel*, and *mercury* salts were prepared.

2-Methylpyrazine-5-carboxylic acid is obtained by oxidising 2:5-dimethylpyrazine with sufficient potassium permanganate to oxidise only one of the methyl groups; it forms lustrous laminæ and prisms (measurements given), melts with decomposition at 200° , and dissolves in hot water, alcohol, and hot benzene. It sublimes very readily, and gives a yellow colour with ferrous sulphate. Its salts are for the most part soluble, the most characteristic being the *silver salt*, which crystallises in long, slender needles.

2:5-Dimethylpyrazine-3-carboxylic acid is the first product of oxidation of dimethylethylpyrazine, and is prepared by limiting the quantity of potassium permanganate to that necessary to oxidise the ethyl group. It crystallises in prismatic needles with $1\text{H}_2\text{O}$, melts, when anhydrous, at 117° , and sublimes undecomposed. It dissolves in hot water, alcohol, ether, chloroform, and benzene, and gives a yellow colour with ferrous sulphate. A *platinochloride* was crystallised, and the *ammonium*, *calcium*, *barium*, *tin*, *lead*, and *mercury* salts were prepared, and found to be soluble in water; the *cobalt*, *nickel*, and *copper* (with $4\text{H}_2\text{O}$) salts are only sparingly soluble; the *silver salt* is very sparingly soluble. The constitution of the acid is settled by the production of 2:5-dimethylpyrazine when it is heated with glacial acetic acid at $180\text{--}200^\circ$ in a sealed tube.

2:5-Pyrazinedicarboxylic acid has been already described as diazinedicarboxylic acid (Abstr., 1892, 507).

Pyrazinetricarboxylic acid is obtained in small quantity during the oxidation of dimethylethylpyrazine; it crystallises in colourless needles with $1\text{H}_2\text{O}$, and becomes red on exposure to air. It melts at $250\text{--}251^\circ$ with decomposition.

α -2:5-Dimethylpiperazine, $\text{NH} \begin{smallmatrix} \text{CHMe}\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CHMe} \end{smallmatrix} \text{NH}$, is obtained by the action of sodium in alcohol on dimethylpyrazine. It crystallises in prisms and tables, melts at 118° , and dissolves in water and alcohol, but not in ether. It is very volatile, and boils at 162° (mercury column in vapour, 746.5 mm.). An aqueous solution of the base, like ammonia, precipitates many metallic oxides. The *hydrochloride*, $\text{C}_6\text{H}_{14}\text{N}_2\cdot 2\text{HCl}$, forms prismatic crystals, and is very soluble in water; it sublimes unchanged when sharply heated. The *hydrobromide* is also described; the crystallography of both salts is given. The *sulphate*, $\text{C}_6\text{H}_{14}\text{N}_2\cdot \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$, crystallises in lustrous prisms very soluble in water. The *dichromate*, $\text{C}_6\text{H}_{14}\text{N}_2\cdot \text{H}_2\text{Cr}_2\text{O}_7$, the *phosphates*, $3\text{C}_6\text{H}_{14}\text{N}_2\cdot 2\text{H}_3\text{PO}_4$, and $\text{C}_6\text{H}_{14}\text{N}_2\cdot 2\text{H}_3\text{PO}_4$, and the *tartrate*, $\text{C}_6\text{H}_{14}\text{N}_2\cdot \text{C}_4\text{H}_6\text{O}_6 + 3\text{H}_2\text{O}$ (m. p. of anhydrous salt $242\text{--}243^\circ$) all

crystallise well, and are crystallographically described. The *platinochloride*, $C_6H_{14}N_2, H_2PtCl_6$, crystallises both in an anhydrous form and with 2 or with 3 mols. of water. The *aurochloride*, $C_6H_{14}N_2, 2HAuCl_4$, is sparingly soluble. The *mercury chloride*, $C_6H_{14}N_2, 2HCl, 4HgCl_2$, crystallises in lustrous, prismatic needles, and melts with decomposition at $235-236^\circ$; its crystallography is detailed. The *picrate*, $C_6H_{14}N_2, 2C_6H_3N_3O_7$, forms sparingly soluble, yellow needles. The *bismuthiodide* is a red, crystalline powder, soluble in water. The *dinitrosamine*, $C_6H_{12}N_2(NO)_2$, obtained by the action of sodium nitrite on the hydrochloride in hydrochloric acid, crystallises in prisms or needles, melts at 172° , and dissolves in water, alcohol, chloroform, and, less easily, in water. The *dibenzoyl* derivative, $C_6N_2H_{12}Bz_2$, obtained by shaking the aqueous solution of the hydrochloride with sodium hydroxide and benzoic chloride, crystallises from alcohol in lustrous rhombohedra, and melts at 225° ; the crystallography is detailed.

The 2 : 5-dimethylpiperazine prepared from ketine appears to be identical with that just described.

Dimethylpiperazylldihydrazine, $NH_2 \cdot N < \begin{smallmatrix} CH_2 \cdot CHMe \\ CHMe \cdot CH_2 \end{smallmatrix} > N \cdot NH_2$, is obtained by reducing the above-described dinitrosamine with zinc-dust and acetic acid, and distilling with alkali; it crystallises in lustrous, stellate prisms with $6H_2O$; it sublimes readily in the form of prisms which melt at $110-111^\circ$, and dissolves easily in water, but less freely in other solvents. The *hydrochloride* forms rhombohedral, or hexahedral crystals, melts with decomposition at 225° , and is sparingly soluble in alcohol and water. The *picrate* is sparingly soluble, and forms small, yellow needles.

β -*Dimethylpiperazine* occurs together with α -2 : 5-dimethylpiperazine, from which it is separated by the greater solubility of its *hydrochloride* in absolute alcohol. The free base crystallises in dazzling, white laminæ, and boils at $161-162^\circ$. The *platinochloride* does not crystallise with water. The *aurochloride* crystallises with $3H_2O$, the measurements of the crystals being given. The *mercury chloride* is $C_6H_{14}N_2, 2HCl, 5HgCl_2$. The *dinitrosamine* crystallises in large, thin laminæ, melts at $95-96^\circ$, and is sparingly soluble in water, but much more soluble in alcohol than the dinitrosamine of the α -base. The *dibenzoyl* derivative is also more soluble in alcohol than is that of the α -base; it crystallises in lustrous tables, and melts at $151-152^\circ$. The author discusses the possible difference in structure between these two bases.

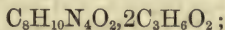
2 : 5-Dimethyl-3-ethylpiperazine, $HN < \begin{smallmatrix} CHMe \cdot CHEt \\ CH_2 - CHMe \end{smallmatrix} > NH$, prepared by reducing the corresponding pyrazine with sodium in alcohol, crystallises (with water) in lustrous prisms; it melts in its water of crystallisation at 62° , and boils at $173-174^\circ$, but the melting and boiling points of the anhydrous base have not been ascertained; it dissolves in water and benzene, but not in ether. The *hydrochloride*, $C_8H_{18}N_2, 2HCl$, is easily soluble in water, but sparingly in alcohol; it sublimes easily. The *platinochloride*, $C_8H_{18}N_2, H_2PtCl_6 + 3H_2O$, is described, and crystallographical measurements of it are given. The

picrate crystallises in yellow needles or laminæ. The *dinitrosamine* crystallises in flat needles, and melts at 92° .
A. G. B.

Constitution of Nicotine. By F. BLAU (*Ber.*, **26**, 1029—1034).—After replying to Pinner's criticism (this vol., i, 443) of his previous paper, the author points out that on the reduction of nicotine by Liebrecht's method, a mixture of hexahydronicotine and octohydronicotine is obtained; the latter is a diimide base, and on treating the hydrochloride with nitric acid, it yields *dinitroso-octohydronicotine*, $C_{10}H_{20}N_2(NO)_2$; the corresponding dibenzenesulphonic derivative, $C_{10}H_{20}N_2(SO_2Ph)_2$, is crystalline, and melts at 143.5° ; it appears to be identical with the corresponding compound (m. p. $133-134^{\circ}$) stated by Pinner to be derived from hexahydronicotine.

Hexahydronicotine is separated from the octohydrogenated base by fractional precipitation of the platinochlorides, of which the latter is the more soluble, and contains a secondary and a tertiary nitrogen atom; it boils at $244.5-245.5^{\circ}$ (corr.), crystallises when anhydrous, and melts at about blood heat. The *hydrochloride* is hygroscopic; the *platinochloride* melts at $226-228^{\circ}$ with decomposition; the *aurochloride* darkens at 175° , and decomposes at $190-191^{\circ}$; the *picrate* is crystalline. The *nitroso-derivative*, $C_{10}H_{19}N_2 \cdot NO$, is soluble, and yields a *platinochloride* which decomposes at $150-152^{\circ}$, and a crystalline *picrate* melting at 140° . In the purification of hexahydronicotine, a base is obtained which has the formula $C_{11}H_{22}N_2$, and boils at $243-245^{\circ}$; its *platinochloride* resembles that of hexahydronicotine in properties and appearance.
J. B. T.

Salts of Caffèine. By E. SCHMIDT (*Arch. Pharm.*, **231**, 1—10).—Since the existence of salts of caffèine has recently been called in question by Tanret, the matter has been again investigated, and the following salts prepared. Their preparation is a little difficult, as they are readily decomposed by water. The *nitrate*, $C_8H_{10}N_4O_2 \cdot HNO_3$, forms large, colourless tables: the *sulphate*, $C_8H_{10}N_4O_2 \cdot H_2SO_4$, rosette-shaped groups of white needles which, on exposure to the air, take up $1H_2O$; the *acetate*, $C_8H_{10}N_4O_2 \cdot 2C_2H_3O_2$; the *propionate*,



the *citrate*, $C_8H_{10}N_4O_2 \cdot C_6H_8O_7$, forms cauliflower-like groups of crystals; the *formate*, *butyrate*, *isobutyrate*, and *isovalerate* could not be obtained pure.
C. F. B.

Papaverine Ethobromide. By A. CLAUS (*J. pr. Chem.* [2], **47**, 523—531).—The author has reinvestigated the crystallography of papaverine ethobromide (Beckenkamp, *Zeit. Kryst. Min.*, **12**, 161; Foullon, *Monatsh.*, 1889, **10**, 684), and finds that the observed difference in crystalline form between different batches does not depend on whether the ethobromide has been made from purified or unpurified papaverine.

Two bases are obtainable by treating the ethobromide with alkalis; the one is colourless, and soluble in water, but not in ether; the other is yellow, and soluble in ether; the action of silver oxide yields the

former. The decomposition occurs in the cold, in which respect papaverine alkyl haloïds differ from those of narceïne and the cinchona alkaloids. The resemblance between papaverine and isoquinoline in the same connection must be noted. A. G. B.

Alkaloids of the Papaveraceæ. By E. SCHMIDT, G. KOENIG, and W. TIETZ (*Arch. Pharm.*, **231**, 136—183).—In the introduction to the paper, a list is given of the alkaloids known to occur in plants of this order, and the physiological properties of these alkaloids are described. There follows, then, a detailed account of the

Alkaloids of the root of Sanguinaria canadensis, for the method of separating which reference must be made to the original paper.

Chelerythrine, $C_{19}H_{11}(OMe)_2NO_2$, is the main constituent. It forms small, colourless, rhombohedral crystals of the formula $C_{19}H_{11}(OMe)_2 + EtOH$, often united in crusts, melts at 203° , has a blue fluorescence, and yields yellow salts. The *hydrochloride*, $C_{21}H_{17}NO_4 \cdot HCl (+ 5H_2O)$ from water, $+ 4H_2O$ from alcohol), *hydriodide*, and *platinochloride* form yellow needles, the *aurochloride* brown needles.

Sanguinarine, $OMe \cdot C_{19}H_{12}NO_3 + H_2O$, forms bundles of white needles or nodular aggregates, melts at 213° , has a bluish-violet fluorescence, and yields blood-red salts. The *hydrochloride*, $C_{20}H_{15}NO_4 \cdot HCl$ (from water, $5H_2O$?; from alcohol, $2H_2O$?), and *nitrate* with $1H_2O$, form red needles, the *platinochloride* a yellow, and the *aurochloride* a reddish-brown, amorphous powder.

γ -*Homochelidonine*, $C_{19}H_{15}(OMe)_2NO_3$, crystallises from ethylic acetate ($+ \frac{1}{2}CH_3 \cdot COOEt$) in large, colourless plates, melts at 169° when quite dry, when air-dried at 159 — 160° , and yields colourless salts. The *platinochloride* forms a yellow, the *aurochloride* a yellowish-red powder. The alkaloid is apparently a tertiary base, for it yields a *methiodide*, $C_{21}H_{21}NO_5 \cdot MeI$, which, with moist silver oxide, yields a hydroxide, from which a *platinochloride*, $(C_{21}H_{21}NO_5)_2 \cdot Me_2PtCl_6$, was obtained as a yellow, amorphous powder.

β -*Homochelidonine*, $C_{21}H_{21}NO_5$, forms bundles of lustrous needles, melts at 159° , and yields colourless salts.

Sanguinaria-protopine, $C_{20}H_{17}NO_5$, crystallises in two interconvertible forms—in white, nodular aggregates and colourless, lustrous, monoclinic prisms; it melts at 207° , and forms colourless salts. The *platinochloride*, with $4H_2O$, is yellow, the *aurochloride* a reddish-brown, amorphous powder.

The *protopine of the root of Chelidonium majus* (*Chelidonium-protopine*) has been again prepared; it melts at 204° , and it and its *platinochloride* and *aurochloride* (melting at 198°) seem to be identical with the compounds obtained from *Sanguinaria protopine*.

The *chelerythrine of the root of Chelidonium majus* has been again prepared, and seems identical with the alkaloid obtained from *Sanguinaria canadensis*. Both these alkaloids melt at 203° , and their *aurochlorides*, melting at 233° , and *platinochlorides* are identical.

C. F. B.

Crystallised Veratrine. By E. MERCK (*Arch. Pharm.*, **231**, 135). Merck's "Veratrine cryst." is identical with the "cevadine" of other authors. It forms white crystals of the composition $C_{32}H_{49}NO_9 +$

$\alpha\text{H}_2\text{O}$, melts when anhydrous at 202° , and yields a crystallised aurochloride, platinochloride, and picrate. C. F. B.

The Relation between Atropine, Apotropine, and Belladonnine. By E. MERCK (*Arch. Pharm.*, **231**, 110—115).—A further proof of the identity of Hesse's atropamine (Abstr., 1891, 228, 748; 1892, 1428) with apotropine is given; the latter, when evaporated with fairly concentrated hydrochloric acid, is converted, like atropamine, into a substance which yields a platinochloride and an aurochloride identical with those of the belladonnine contained in the mother liquor that is obtained in the preparation of atropine. Apotropine, which is formed from atropine by loss of water, is thus converted by dilute acids into belladonnine. C. F. B.

Hyoscyamine. By E. MERCK (*Arch. Pharm.*, **231**, 115—117).—Hyoscyamine, $[\alpha]_D = -20.25^\circ$, when heated for a few hours with water in an open vessel at 100° , yields, besides atropine and unaltered hyoscyamine, inactive tropine and crystallised levorotatory tropic acid ($[\alpha]_D = -7.5^\circ$ and -15° in two separate preparations); Ladenburg and Hundt (Abstr., 1890, 74) describe this acid as an amorphous, yellow powder with $[\alpha]_D = -65.15^\circ$.

Hyoscyamine and hyoscyne hydrobromides dissolve respectively in 0.34 and 4 parts of water at 15° , and in 2.2 and 21.5 parts of alcohol (sp. gr. = 0.820). C. F. B.

Pseudohyoscyamine. By E. MERCK (*Arch. Pharm.*, **231**, 117—123).—This new alkaloid occurs in *Duboisia myoporoides*, together with hyoscyamine and hyoscyne. It forms small, yellowish needles of the composition $\text{C}_{17}\text{H}_{23}\text{NO}_3$, melts at $133\text{--}134^\circ$, and has specific rotation $[\alpha]_D = -21.15^\circ$; the *platinochloride*, with $2\text{H}_2\text{O}$, forms feather-like groups of needles which (when anhydrous?) begin to melt at 116° and decompose below 150° ; the *aurochloride* forms thin, yellow, lustrous plates melting at 176° ; the *picrate* forms yellow needles melting at 220° . (The following *picrates* were prepared for purposes of comparison: from atropine, yellow plates melting at $175\text{--}176^\circ$; hyoscyamine, crusts of needles or quadrangular plates, melting at $161\text{--}163^\circ$; hyoscyne, slender matted needles melting at $160\text{--}162^\circ$.) Pseudohyoscyamine, when hydrolysed by boiling with barium hydroxide in dilute alcohol, yields tropic acid and a base isomeric with atropine; the *platinochloride*, $2\text{C}_8\text{H}_{15}\text{NO}, \text{H}_2\text{PtCl}_6 + \text{H}_2\text{O}$, of this base forms reddish-yellow, crystalline masses which become discoloured at 210° , and get gradually blacker as the temperature rises. C. F. B.

Hydrastine Hydrogen Tartrate. By E. MERCK (*Arch. Pharm.*, **231**, 134—135).—*Hydrastine hydrogen tartrate*,



is the first simple salt of this base which has been obtained crystallised. It forms white needles, and can be advantageously utilised for the purification of hydrastine. C. F. B.

Alkaloïds from *Corydalis cava*. By E. MERCK (*Arch. Pharm.*, **231**, 131—134).—The following alkaloïds occur in the roots of this plant; they are arranged in descending order of relative amount: (1) *Bulbocapnine*, melting at 199° ; (2) *Corydine*, an amorphous substance which produces violent epilepsy, terminating fatally when administered hypodermically to a cat; (3) *Corydaline*, melting at 135° ; (4) a base (? *Corycavine*), which crystallises in small, matted needles and melts at 218° . The first two are more pronouncedly basic than the last two (compare Dobbie and Lauder, *Trans.*, 1892, 244, 605; 1893, 485).
C. F. B.

Gelseminine. By L. SPIEGEL (*Ber.*, **26**, 1054—1060).—Pure gelseminine from *Gelsemium sempervirens*, is amorphous, softens at 105° , and melts at about 120° with partial decomposition; it is precipitated from its salts by ammonia, alkalis, and alkali carbonates, and is soluble in excess of these reagents; it is not altered by fusion with potassium hydroxide. The *hydrochloride* crystallises in concentric prisms which darken at 330° without melting; the *hydrobromide* and *hydriodide* are crystalline and unstable; the *sulphate* is amorphous; the *nitrate* is deposited from alcohol in strongly refractive octahedra or tetrahedra, and melts at 188° with decomposition. The *platinochloride* is yellow and probably amorphous; the *aurochloride* is also amorphous and brown in colour.

Gelseminine does not contain any methoxy-groups, as is shown by its behaviour towards hydriodic acid; with phenylhydrazine, a crystalline compound is formed in small quantity, but has not been investigated.

Gelseminine methiodide crystallises with $2\text{H}_2\text{O}$ and melts at 285° with decomposition; it does not react with alkalis but is decomposed by silver oxide yielding an amorphous substance. On fusion with potash, the methiodide is resolved into two nitrogenous bases, one of which is volatile, has a fishy smell, and yields a crystalline *hydrochloride*.

Gelseminine yields two products on oxidation with potassium permanganate; the one is yellowish-brown and amorphous, the other is a colourless acid; both are being further investigated. With dilute nitric acid, the base yields a number of brown indefinite products together with an acid, $\text{C}_{17}\text{H}_{20}\text{N}_3\text{O}_8$, which is deposited from alcohol in pale yellow crystals; it darkens at 350° without melting, and is not acted on by concentrated nitric acid. The brown compounds, on treatment with concentrated nitric acid, yield a colourless, crystalline substance.

Gelseminine combines with one equivalent of acids; the author has made numerous analyses of the base, the hydrochloride, and the nitrate; his results show that Sonnenschein's formula, $\text{C}_{22}\text{H}_{38}\text{N}_2\text{O}_4$, is incorrect, but they are inadequate to distinguish between the formulæ $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_4$ and $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_3$. The identity or otherwise of gelseminine and gelsemine is also undetermined.
J. B. T.

Organic Chemistry.

Recognition of Paraffin and of Lubricating Oil in the Distillate of Train Oil under Pressure. By C. ENGLER and L. SINGER (*Ber.*, 26, 1449—1451).—The higher-boiling portions of the distillate were extracted with sodium hydroxide solution to remove any undecomposed fatty compounds, and allowed to remain in a freezing mixture for a week, when a solid, crystalline paraffin separated; when dissolved in light petroleum, and the solution poured into 75 per cent. alcohol, it was obtained as a white, crystalline mass; it melted at 49—51°.

To isolate the lubricating oil, the crude distillate was shaken successively with sodium hydroxide solution, water, sulphuric acid, and then again with water; after fractional distillation, the fractions were shaken successively with concentrated sodium hydroxide solution, water, sulphuric acid, water, sodium hydroxide and water, and again distilled. The heavy oil was of a yellowish-brown colour, and exhibited a strong fluorescence after washing with sodium hydroxide solution. The specific viscosity of the fraction boiling at 290—300° was 1·6 at a temperature of 50—60°, water being taken as unity, and that of a fraction boiling above 300° was 3·4. The constitution of these high-boiling oils could not be determined, and it was not, therefore ascertained whether they were identical with the synthetic products of Krämer and Spilker (*Abstr.*, 1891, 1462).

A. R. L.

Licarene from Licareol. By P. BARBIER (*Compt. rend.*, 116, 993—994).—When licareol (*Abstr.*, 1892, 1236, and this vol., i, 495, 496) is heated with acetic anhydride at 150°, it yields *licarene*, $C_{10}H_{16}$, a very mobile liquid with an agreeable odour. This boils at 176—178° under ordinary pressure; sp. gr. at 0° = 0·8445; index of refraction for λ 645 = 1·4741, and for λ 452·6 = 1·4922, at 17°. At 20·2° its rotatory power $[\alpha]_D = +7^\circ 51'$, and is, therefore, opposite in sign to that of licareol. Licarene combines with bromine to form a mixture of a liquid and a solid tetrabromide, the latter melting at 103—104°. When treated with chromic mixture, it yields terpenylic acid and acetic acid. When treated with dry hydrogen chloride in acetic acid solution, it yields an inactive *dihydrochloride* boiling at about 155° under a pressure of 39 m.; sp. gr. at 0° = 1·0446; index of refraction for λ 645 = 1·4819, and for λ 452·6 = 1·4948. The same dihydrochloride is obtained by the direct action of hydrogen chloride on licareol.

Licarene yields a crystalline nitrosochloride, $C_{10}H_{16}NOCl$, and this, when boiled with alcoholic potash, yields nitrosolimonene or carvoxime. It would seem from this and the other properties that licarene belongs to the limonenes of Wallach. The latter form crystalline dihydrochlorides, but licarene dihydrochloride is probably a stereoisomeride.

C. H. B.

Constitution of Dicyanodiamide. By E. BAMBERGER and L. SEEBERGER (*Ber.*, **26**, 1583—1587).—Between the constitutional formulæ proposed by Baumann and by Bamberger for dicyanodiamide, namely, $\text{NH:C} < \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} > \text{C:NH}$ and $\text{NH:C}(\text{NH}_2) \cdot \text{NH} \cdot \text{CN}$, the experimental data have been hitherto insufficient to decide. The authors have now found that if dicyanodiamide is subjected to the continued action of zinc and dilute hydrochloric acid at the ordinary temperature, it is converted into guanidine and methylamine, the latter being probably formed by the reduction of the hydrogen cyanide first produced. To obtain direct evidence of the formation of the latter, dicyanodiamide was boiled with hydroxylamine in aqueous solution; carbonic anhydride and nitrous oxide were evolved, and the product was found to consist chiefly of a little ammeline and large quantities of guanylcarbamide. If the solution remaining after the evolution of gas has ceased was acidified with sulphuric acid and warmed, hydrogen cyanide was evolved.

The direct formation of guanidine and hydrocyanic acid shows that Bamberger's formula is correct, and that dicyanodiamide is in reality cyanoguanidine; its formation from cyanamide is, therefore, similar to that of aldol from acetaldehyde and to the polymerisation of methylic cyanide.

To detect dicyanodiamide, the best method is to boil with dilute acetic acid, which, like other acids, converts it into guanylcarbamide; the solution is then treated with soda and a small quantity of copper sulphate solution, when, if dicyanodiamide is present, pink crystals of copper guanylcarbamide separate, or if the quantity is small the biuret coloration is produced; the absence of biguanide, biuret, and guanylcarbamide from the original substance must first be ascertained.

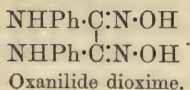
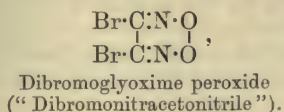
H. G. C.

Structure of Fulminates. Dibromonitracetonitrile. By A. F. HOLLEMAN (*Ber.*, **26**, 1403—1408).—The author first gives reasons for preferring his own formula, $\text{Hg} < \begin{smallmatrix} \text{C:N} \cdot \text{O} \\ \text{C:N} \cdot \text{O} \end{smallmatrix} >$, for mercury fulminate

to that of Steiner, $\begin{smallmatrix} \text{C:NO} \\ \text{C:NO} \end{smallmatrix} > \text{Hg}$, recently advocated by Scholl (*Abstr.*, 1891, 283), and then proceeds to describe a new product which he has obtained from dibromonitracetonitrile.

When dibromonitracetonitrile is heated with aniline in the water-bath, there is obtained a small quantity of a substance which crystallises in square plates melting with decomposition at 215° , and yields a *diacetyl* derivative melting, with decomposition, at a little above 200° , and a *dibenzoyl* derivative which begins to melt, with decomposition, at about 120° . This substance must be *oxanilide dioxime*, for, when heated with hydrochloric acid at 130° , it yields oxanilide and hydroxylamine, together with the decomposition products of the former, oxalic acid, and aniline. Dibromonitracetonitrile thus yields oxanilide dioxime, and must, consequently, be regarded as dibromoglyoxime peroxide. A further consequence is that mercury fulminate, from

which dibromonitracetonitrile may be obtained, must have the constitution assigned by the author,



C. F. B.

Ethereal Hydrogen Sulphates from Secondary Alcohols. By T. R. KRÜGER (*Ber.*, 26, 1203—1204).—*Ethylpropylcarbinyllic hydrogen sulphate*, $\text{CH}_3\text{EtPr}^a\text{OSO}_3\text{H}$, is prepared by mixing ethylpropylcarbinol, prepared from the corresponding ketone, with sulphuric acid: the mixture is cooled for some hours, then heated to 40—50°, and diluted with water; from this solution the *barium salt*, $(\text{C}_6\text{H}_{13}\text{SO}_4)_2\text{Ba}$, is obtained in the ordinary manner; it is somewhat unstable, readily soluble in water or alcohol, and crystallises from the latter in colourless needles. The salt is not precipitated from its aqueous solution by the addition of ether, chloroform, or light petroleum.

The *strychnine salt* crystallises in monoclinic or rhombic plates; the *morphine salt* is unstable.

The constitution of the salts is shown by the fact that barium sulphate is formed on heating the strychnine salt with hydrochloric acid and barium chloride, or the barium salt with hydrochloric acid alone.

The statement that secondary alcohols do not form ethereal hydrogen sulphates thus requires modification. Bonis has previously prepared a compound of this class from methylhexylcarbinol, but the alcohol had been obtained from castor oil and may have been impure.

J. B. T.

Derivatives of Licareol. By P. BARBIER (*Compt. rend.*, 116, 883—884).—Licareol (*Abstr.*, 1892, 1236) in a well cooled acetic acid solution combines directly with bromine, yielding an almost colourless, viscous tetrabromide, and the latter, when treated with silver hydroxide, yields a product in which the bromine has been displaced by hydroxyl.

When large quantities of licareol are oxidised, a compound of the composition $\text{C}_{10}\text{H}_{16}\text{O}$ is obtained. It is a colourless, slightly viscous liquid with an agreeable odour of citron. It boils at 118—120° under a pressure of 20 mm. and at about 224—226°, with decomposition, under the ordinary pressure; sp. gr. at 0° = 0.9119; index of refraction for λ 645 = 1.4736, and for λ 452.6 = 1.4907 at 17.8°. This compound, *licaraldehyde*, has no action on polarised light; it forms a crystalline compound with sodium hydrogen sulphite, reduces energetically an ammoniacal solution of silver nitrate, and, when treated with sodium hypobromite in presence of potassium iodide, yields no iodoform. With hydroxylamine, it yields an oily oxime, $\text{C}_{10}\text{H}_{17}\text{NO}$, which has an aromatic odour, and boils at about 150° under a pressure of 15 m.m., with slight decomposition. If this oxime is boiled for some time with acetic anhydride, it yields *licaronitrile*, $\text{C}_{10}\text{H}_{15}\text{N}$, a colourless liquid with an aromatic odour, which boils at 137—138°

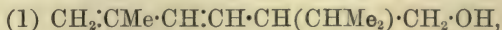
under a pressure of 15 mm. When the nitrile is boiled with concentrated alcoholic potash, *licaric acid*, $C_{10}H_{16}O_2$, is obtained. This acid is also obtained in smaller quantity by the oxidation of licareol by potassium permanganate in neutral solution. It is an oily liquid, with a strong and disagreeable odour; it is only slightly soluble in water, but dissolves in ether. The barium salt is gummy; the silver salt is white and only slightly soluble in water.

When oxidised by chromic mixture, licareol yields, in addition to licaldehyde, formic and acetic acids and a trace of butyric acid.

It would follow, therefore, that licareol is a primary alcohol which can be represented by the formula $C_9H_{15} \cdot CH_2 \cdot OH$, the residue, C_9H_{15} , containing two ethylenic bonds, and being an open-chain hydrocarbon.

C. H. B.

Constitution of Licareol. By P. BARBIER (*Compt. rend.*, 116, 1062—1064; compare preceding abstract).—The conversion of licareol into an active limonene, licarene, and the formation from it of carvoxime melting at 72° , indicates the presence of the groups $\cdot CH:CH \cdot$. The relation between carvoxime, carvol, and carvacrol indicates the existence of the groups $CHMe_2 \cdot$ and $Me \cdot$, and hence it would follow that licareol has the constitution



or (2) $CH_2 \cdot C(CHMe_2) \cdot CH:CH \cdot CHMe \cdot CH_2 \cdot OH$. A compound with the first constitution should yield valeric acid on oxidation, but licareol and licaldehyde yield formic and acetic acids and a small quantity of isobutyric acid, but no valeric acid. It would seem, therefore, that the second formula is probably correct, and the constitution of licarene

(this vol., i, 493) will be $CPr^{\beta} \begin{matrix} CH \cdot CH_2 \\ \diagup \quad \diagdown \\ CH:CH \end{matrix} > CHMe$. C. H. B.

Trehalum, a new Carbohydrate. By C. SCHEIBLER and H. MITTELMEIER (*Ber.*, 26, 1331—1336).—When the residue obtained in the preparation of trehalose from trehala manna is extracted with boiling water and filtered, a crystalline precipitate of a new carbohydrate separates out in the course of 24 hours; it may be purified by washing with cold, and recrystallising from hot, water, and then forms a fine, lustrous, white, very hygroscopic powder, consisting of microscopic prisms. It appears to have the composition $C_{24}H_{42}O_{21}$, is tasteless and odourless, scarcely soluble in cold, more readily in hot, water, and, on cooling, forms supersaturated solutions. It is dextro-rotatory, $[\alpha]_D = +179^\circ$. It only reduces Fehling's solution after boiling with acids, and yields *d*-glucose as the sole recognisable product of hydrolysis.

Trehalum does not melt at 240° , but becomes slightly yellow when heated for two hours at 180° , and the product is then readily soluble in water; on addition of alcohol to the solution, a precipitate is thrown down, which may be obtained crystalline by dissolving in water and allowing the solution to remain. The product, unlike the original substance, dissolves in phenylhydrazine, and is therefore an aldehyde. The two compounds thus behave in an analogous manner

to starch and dextrin, and the authors, therefore, propose to term them *trehalum* and *trehalin*.

When iodine is added to a mixture of trehalum and water, the particles of trehalum are coloured violet and the solution wine-red; on warming, the colour disappears, and, on again cooling, the solution assumes a deep violet colour. Trehalin is coloured reddish-violet by iodine in aqueous solution.

Trehalum is not acted on by diastase, yeast, or invertase, but always undergoes slight hydrolysis when heated even to 105°, as shown by the action of the product on Fehling's solution. It yields an acetyl derivative which melts above 240°, but shows no characteristic properties.

H. G. C.

Inulase, and the Indirect Alcoholic Fermentation of Inulin.

By E. BOURQUELOT (*Compt. rend.*, **116**, 1143—1145).—*Aspergillus niger*, when grown on a nutritive fluid containing inulin, produces a ferment capable of converting dilute solutions of inulin practically completely into levulose. This ferment is distinct from invertin and amylase, because neither of the latter has any action on inulin, and it differs from trehalase because it retains its activity after being heated at 64°. It seems to be identical with the inulase obtained by Green from one of the plants that yield inulin.

If inulin solution is mixed with inulase and beer yeast, it undergoes alcoholic fermentation, the inulase converting it into levulose, which is then attacked by the yeast.

C. H. B.

Tunicin. By E. WINTERSTEIN (*Zeit. physiol. Chem.*, **18**, 43—56).—Tunicin, or animal cellulose, agrees in nearly all its properties with vegetable cellulose. It does not show greater resistance to acids than vegetable cellulose, as Berthelot stated. On hydrolysis, it yielded dextrose, and a small quantity of another sugar, which was not identified. This second sugar is, however, not galactose, mannose, or pentose.

W. D. H.

Chloramines. By A. BERG (*Compt. rend.*, **116**, 887—889).—Methylchloramine is obtained by the action of sodium hypochlorite on methylamine hydrochloride. It is practically colourless, very volatile, has an extraordinarily piquant and irritating odour, and dissolves in water to the extent of about 10 per cent. by volume. Dimethylchloramine is obtained in a similar manner; it is almost colourless, has a very piquant odour, dissolves in about 8 parts of water by volume, and boils at 46° under a pressure of 765 mm.; sp. gr. at 0° = 0.986. When treated with potassium cyanide, energetic reaction takes place, and dimethylcyanamide and tetramethylcarbamide are obtained. The former boils at 163.5° under a pressure of 760 mm. The latter is formed by the hydration of a tetramethylguanidine produced by the action of the dimethylcyanamide on regenerated dimethylamine hydrochloride.

The ethylamines, when treated in a similar manner, yield analogous products.

When an aqueous solution of methylchloramine is mixed with a

solution of potassium iodide, a maroon-red, unstable precipitate is formed, which seems to be methyl iodamine. Dimethylchloramine and propylchloramine behave in the same way. With the dichloramines and the monochloramines, which are less soluble in water, the reaction is less distinct.

Amyldichloramine and diamylchloramine, when distilled with water and acetic or sulphuric acid, yield only the merest traces of hypochlorous acid (compare Selivanoff, this vol., i, 305). C. H. B.

Action of Alkalis on Betaine. By C. SCHEIBLER (*Ber.*, 26, 1330—1331).—Many years ago the author showed that when betaine was treated with a large excess of potash and a little water, it gave off trimethylamine, whilst the residue yielded a base which appeared not to be identical with betaine. Further experiments with larger quantities of betaine, in which soda was substituted for potash, have shown, however, that, with the exception of trimethylamine, no new base is formed, the substance obtained with potash being probably impure betaine. H. G. C.

Condensation Products of Acetone with Concentrated Sulphuric acid. By W. R. ORNDORFF and S. W. YOUNG (*Amer. Chem. J.*, 15, 249—276).—The materials employed in this investigation consisted of 6.84 kilos. of acetone and 12.6 kilos. of sulphuric acid, which were very cautiously heated together in small quantities to a temperature of 140°. The chief product was mesitylene, of which over 11.5 per cent. of the theoretical yield was obtained, and this was accompanied by a not inconsiderable quantity of isodurene. A compound boiling at 183—185°, and having the formula $C_{14}H_{22}O$, was a constant product of the reaction. It is a light, colourless, mobile liquid, with quite a marked aromatic odour; its specific gravity at 0°, compared with water at 4°, is 0.8865. From the tarry products, a hydrocarbon, boiling at 280—282°, and having the formula $C_{15}H_{20}$, was obtained. It is a viscous liquid, with a yellow colour and very little odour, and, in all probability, is a polymeride of allylene. In addition to the substances above named, propane, sulphurous anhydride, acetic acid, mesityl oxide, phorone, and sulphur compounds were produced.

Regarding the method by which mesitylene is formed from acetone, the authors are of the opinion that the acetone first unites with the sulphuric acid, forming an additive product, exactly as it does with hydrocyanic acid; the additive product loses water, yielding the acid sulphate of isopropenyl alcohol, $CH_2:CM_e \cdot OH$, which, on hydrolysis, gives rise to sulphuric acid and isopropenyl alcohol, an unstable substance which rapidly changes into acetone by molecular rearrangement. When heated with concentrated sulphuric acid, however, the acid sulphate of isopropenyl alcohol would yield sulphuric acid and allylene, and 3 mols. of the latter condense to form mesitylene. The formation of mesitylene from acetone must, therefore, very closely resemble the formation of ethylene from alcohol, and, in support of this view, it may be noted that when acetone and sulphuric acid are mixed, so much heat is evolved that it is necessary to cool with ice-water the flask in which the two liquids are mixed. The mixture is

thick and oily, and has entirely lost the odour of acetone. When distilled with a large excess of water, almost all the acetone used may be recovered.
G. T. M.

Ketoximes. By C. TRAPESONZJANZ (*Ber.*, **26**, 1426—1428).—The following ketoximes were obtained by boiling the corresponding ketones with hydroxylamine hydrochloride (1 mol.) and sodium carbonate ($\frac{1}{2}$ mol.) in dilute alcoholic solution. The specific gravities given were determined at 20°, and are referred to water at 4°, being also corrected for a vacuum.

Methylbutylketoxime, $\text{NOH}:\text{CMe}:\text{CH}_2\text{Pr}^\alpha$, is a colourless liquid, boiling at 185° under 757 mm., and at 138° under 112 mm. pressure; sp. gr. = 0.8971.

Methylisoamylketoxime, $\text{NOH}:\text{CMe}:\text{CH}_2:\text{CH}_2\text{Pr}^\beta$, is a colourless liquid of agreeable odour, boiling with partial decomposition at 195—196° under 761 mm. pressure; sp. gr. = 0.8881.

Ethylphenylketoxime, $\text{NOH}:\text{CEtPh}$, forms mono- or tri-clinic crystals, melting at 52—53°, and boils at 165° under 35 mm. pressure, at 245—246° with partial decomposition at the ordinary pressure. Pampel and Schmidt (*Abstr.*, 1887, 252) have already obtained it, but only as an oil.

The *ethyl derivative* of *methylphenylketoxime*, $\text{NOEt}:\text{CMePh}$, was obtained by treating a solution of sodium in absolute alcohol successively with acetophenonoxime and ethylic iodide; it is a colourless oil, boiling at 200—202° under 43 mm. pressure; sp. gr. = 0.9997.

C. F. B.

Behaviour of Trichloroacetic acid at a High Temperature. By C. ENGLER and M. STEUDE (*Ber.*, **26**, 1443—1444).—When trichloroacetic acid is heated at 300°, it decomposes into trichloroacetic chloride, carbonic anhydride, carbonic oxide, and hydrogen chloride. This decomposition cannot be used as an argument against the rule previously given (this vol., i, 512), as, in this case, the tendency to form hydrogen chloride brings about a decomposition in another direction.
A. R. L.

Application of the Dynamical Hypothesis to Keto-acid Derivatives. By C. A. BISCHOFF and P. WALDEN (*Ber.*, **26**, 1452—1460).—According to Bischoff's "dynamical hypothesis," the formation of lactones from γ -keto-acids should be influenced by the presence of alkyl radicles in the α -position. In order to test this conclusion, weighed quantities of levulinic acid and some of its alkyl derivatives were heated at 275° for different lengths of time, cooled, and titrated with sodium carbonate solution. The following results give the amounts of lactones obtained:—

Acid.	15 minutes.	30 minutes.	45 minutes.	60 minutes.
Levulinic	7.63 p. c.	13.09 p. c.	21.54 p. c.	26.57 p. c.
α -Methyllevulinic	20.48 "	29.85 "	33.99 "	48.88 "
α -Dimethyllevulinic	27.86 "	31.96 "	35.62 "	—
α -Ethyllevulinic	37.24 "	44.26 "	47.95 "	58.63 "

Ethyllic acetosodacetate gives, with ethyllic α -bromopropionate and α -bromonormalbutyrate, ethyllic methylacetosuccinate and ethyl-acetosuccinate, in yields of 60 and 52 per cent. respectively. With ethyllic α -bromisobutyrate, the yield of ethyllic α -dimethylacetosuccinate was found to be only 4 per cent., in accordance with the dynamical hypothesis.

Ethyllic methylacetosodacetate and ethyllic α -bromisobutyrate, when heated with xylene in autoclaves to a pressure of 2.5 atmospheres, yielded an ethereal product, from which, by hydrolysis, tetramethylsuccinic acid and trimethylglutaric acid were obtained.

Paradimethylsuccinic acid is much less easily converted into the anhydride than antidimethylsuccinic acid. J. W.

Action of Alcohols on Lactones and Alkyl Salts. By J. WALKER (*Ber.*, 26, 1492—1493).—In opposition to Brühl, the author shows that lactone rings have been split up by the action of alcohol alone, or together with a halogen acid. The products formed are either an ether acid, the ethereal salt of a hydroxy-acid (or corresponding halogen substituted acid), or, finally, the ethereal salt of an ether acid.

The replacement of one alkyl by another in an ethereal salt corresponds with the second of the above cases, and the author finds that ethyllic oxalate, heated with excess of methyl alcohol at 160°, yields methyllic oxalate, whilst this ethereal salt at the same temperature is converted by ethyl alcohol into ethyllic oxalate. J. W.

Malic acid Derivatives. By P. A. GUYE (*Compt. rend.*, 116, 1133—1136).—Active *acetylmalic anhydride*, obtained by the action of acetic chloride on carefully dried lævogryate malic acid, melts at 58°, dissolves easily in benzene and especially in chloroform, from which it crystallises readily, but is only slightly soluble in dry ether. It rapidly absorbs moisture from the air, and forms acetylmalic acid. The rotatory power of the anhydride in chloroform solution is $[\alpha]_D = -26^\circ$.

Active *acetylmalic acid*, obtained by the crystallisation of a concentrated solution of the anhydride in moist chloroform, has a specific rotatory power $[\alpha]_D$ of -21.0 to -25.8 in acetone, and -10.4 to -10.7 in water. When slowly heated, it softens between 120 and 125°, and melts at 130—131°. When rapidly heated, it melts at a somewhat higher temperature. The fused acid gives off acetic acid, and maleic acid is left. It would seem, therefore, that in the conversion of malic acid into maleic acid by the action of acetic chloride, an acetyl derivative is first formed, but is afterwards decomposed. An aqueous solution of acetylmalic acid gradually decomposes, yielding acetic and malic acids.

Propionylmalic anhydride, obtained in a similar manner, crystallises readily from chloroform, but is almost insoluble in ether. It melts at 88—89°, and its rotatory power in chloroform solution is $[\alpha]_D = -22.1^\circ$ to -20.4° .

Propionylmalic acid, obtained in the same way as the acetyl derivative, is lævogryate in chloroform solution. It crystallises from

chloroform, and at about 130° splits up into propionic and maleïc acids.

Butyrylmalic anhydride and *butyrylmalic acid* are much more difficult to isolate. The former is lævogyrate in chloroform solution, and the latter is likewise lævogyrate when dissolved in aqueous acetone.

C. H. B.

Constitution of Leucine. By B. GMELIN (*Zeit. physiol. Chem.*, 18, 21—42).—Leucine prepared from different sources is not always the same as Schulze and Likiernik (this vol., i, 309) consider. Three preparations were made (1) from yeast, (2) from caseïn, (3) from hæmoglobin. Elementary analysis gave results in each case closely corresponding to the formula $C_6H_{13}NO_2$. Their solubilities in water are however different.

	Solubility in water	
	At 19° .	At about 100° .
Preparation 1	1 in 28·8	1 in 15·9
„ 2	1 in 29·0	1 in 14·3
„ 3	1 in 45·8	1 in 18·7

Their action on polarised light is different. Dissolved in hydrochloric acid, $[\alpha]_D$ for preparations 1 and 2 = $+17\cdot2^{\circ}$, for preparation 3 = $+14\cdot3^{\circ}$. The melting point of leucic acid obtained from preparations 1 and 2 is $72\cdot5^{\circ}$; from preparation 3, 67° . These acids also differ in rotatory power, and in the solubilities of their zinc salts.

The three fatty acids obtained correspond with isobutylacetic acid. The cause of the differences cannot be looked for in the position of the amido-group, and reasons are given for considering that one has to deal with a case of “physical isomerism.”

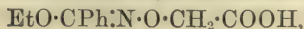
The molecular weights of leucine, glycocine, and alanine estimated by the cryoscopic method correspond closely with those reckoned from their simplest formulæ.

W. D. H.

Hydroxylamineacetic acid. By A. WERNER (*Ber.*, 26, 1567—1571).—The author has previously shown (*Abstr.*, 1892, 461) that benzenylchloroximeglycollic acid exists in two isomeric forms, and has now made further experiments in order to ascertain if possible the stereometric formulæ of the two isomerides. These have been unsuccessful owing to the fact that the products obtained are oils which can scarcely be distinguished from one another. They yield as a product of decomposition hydroxylamineacetic acid,

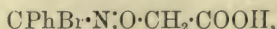


In place of the name benzenylchloroximeglycollic acid, the author prefers to employ the term benzenylchloroximeacetic acid. This acid is obtained in the manner already described from benzenylamidoximeacetic acid, the latter being preferably prepared by treating ethylic chloracetate and benzenylamidoxime with alcohol and potash, instead of soda, as the potassium salt is much less soluble. Both modifications of benzenylchloroximeacetic acid yield, on treatment with sodium ethoxide, an *ethylbenzhydroximeacetic acid*,



both products being syrupy oils which cannot be distinguished one from the other. When treated with hydrochloric acid, they are rapidly decomposed, the products being ethylic benzoate and the *hydrochloride of hydroxylamineacetic acid*, $\text{NH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}\cdot\text{HCl}$; the latter crystallises from alcohol in compact, white needles, and melts at $147-148^\circ$. The free acid appears to be a liquid, and is at present being further investigated.

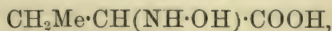
Besides the chloro-derivative the author has converted benzenylamidoximeacetic acid into *benzenylbromoximeacetic acid*,



benzenylfluoroximeacetic acid, $\text{CPhF}\cdot\text{N}\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}$, and *benzenylnitritoximeacetic acid*, $\text{NO}\cdot\text{O}\cdot\text{CPh}\cdot\text{N}\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}$; the first may be crystallised from hot water, and melts at $135-136^\circ$, the second forms nacreous plates, and melts at 135° , and the third crystallises in white, lustrous plates, and melts at $95-96^\circ$. In none of these cases was the formation of stereoisomerides observed. When benzenylnitritoximeacetic acid is warmed for a short time with potash, it is converted into *benzoylhydroxylamineacetic acid* (*benzhydroxamacetic acid*), $\text{NHBz}\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}$ or $\text{OH}\cdot\text{CPh}\cdot\text{N}\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}$, which after crystallisation from ether melts at $135-138^\circ$. H. G. C.

Amidoxylic acids. By W. v. MILLER and J. PLÖCHL (*Ber.*, 26, 1545—1558).—Several methods are known by which α -amido-acids and the corresponding α -isonitroso-acids can be obtained, but hitherto none of the intermediate α -amidoxylic acids having the general formula $\text{OH}\cdot\text{NH}\cdot\text{CHX}\cdot\text{COOH}$ have been prepared. The authors find that the nitriles of these acids may be readily obtained by the addition of hydrogen cyanide to the oximes, and that the nitriles on treatment with hydrochloric acid yield the acids themselves. The latter contain the hydroxylamine residue $\text{NH}\cdot\text{OH}$, and are therefore strong reducing agents, and although they are stronger acids than the amido-acids, no salts can be obtained, for with dilute alkalis ammonia is evolved, and on addition of salts of the heavy metals reduction immediately takes place. On dry distillation, they all decompose with violent evolution of gas, forming carbonic anhydride, ammonia, pyridine bases, and often small quantities of aldehydes. Sulphuric acid cannot be employed in place of hydrochloric acid for the hydrolysis of the nitriles, as oxidation takes place simultaneously under these conditions, the corresponding α -isonitroso-acid being formed.

Propaldoxime and hydrogen cyanide combine together in the cold on remaining for two days, with formation of α -amidoxybutyronitrile, $\text{CH}_2\text{Me}\cdot\text{CH}(\text{NH}\cdot\text{OH})\cdot\text{CN}$, which is a crystalline compound, and melts at $86-87^\circ$; when treated with cold fuming hydrochloric acid, it is converted into α -amidoxybutyric acid,



which forms rhombohedral crystals, and melts at $166-167^\circ$ with violent evolution of gas; the distillate contains, in addition to ammonium carbonate, a small quantity of a pyridine base, apparently

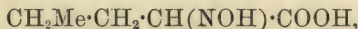
identical with parvoline, which may also be obtained by heating propaldehyde and hydroxylamine hydrochloride at 120° . The acid reduces the salts of the heavy metals quickly in the cold; it also combines directly with aldehydes forming unstable compounds which will be investigated later.

When the nitrile is treated with sulphuric acid, sulphurous anhydride is evolved, and on pouring the product into water α -isonitrosobutyramide, $\text{CH}_2\text{Me}\cdot\text{C}(\text{NOH})\cdot\text{CONH}_2$, separates out, and is purified by dissolving in ether and adding light petroleum. It melts at 133 — 135° , and on hydrolysis yields the α -isonitrosobutyric acid described by Wleügel.

Attempts to prepare the corresponding amidoxylpropionic acid from the nitrile of acetaldoxime were without success, probably owing to the fact that the acid is extremely soluble in water, and could not be isolated. If the nitrile be treated with sulphuric acid, it yields α -isonitrosopropionamide, $\text{CH}_2\text{Me}\cdot\text{C}(\text{NOH})\cdot\text{CONH}_2$, which crystallises in large, apparently monosymmetric tables, melts with decomposition at 178.5° , and is converted by alkalis into the known isonitrosopropionic acid.

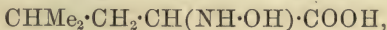
Acetoxime readily combines with hydrogen cyanide, forming amidoxylisobutyronitrile, $\text{CMe}_2\cdot\text{C}(\text{NOH})\cdot\text{CN}$, which crystallises in well-developed, monosymmetric tablets, melts at 98.5° , and yields with hydrochloric acid the hydrochloride of amidoxylisobutyramide, $\text{CMe}_2(\text{NH}\cdot\text{OH})\cdot\text{CO}\cdot\text{NH}_2\cdot\text{HCl}$, which separates in large crystals, and melts at 210° . Attempts to prepare the free amide and the corresponding acid were unsuccessful.

Normal butyraldoxime, which is an oil boiling at 152° under 715 mm. pressure, combines with hydrogen cyanide, forming amidoxylvaleronitrile, $\text{C}_6\text{H}_{10}\text{N}_2\text{O}$, which forms a spongy mass of silky crystals, melts at 102° , and has extremely active reducing properties. With hydrochloric acid, it yields α -amidoxylvaleric acid,



which crystallises in rhombic plates, sinters at 150° , melts at 156° , and is also a very strong reducing agent. With sulphuric acid, the nitrile is converted into isonitrosovaleramide, $\text{C}_6\text{H}_{10}\text{N}_2\text{O}_2$; the latter crystallises in slender needles, melts at 131° , and may be converted in the usual manner into α -isonitrosovaleric acid.

Isovaleraldoxime yields with hydrogen cyanide amidoxylisocapro-nitrile, $\text{C}_8\text{H}_{12}\text{N}_2\text{O}$, crystallising in delicate, white threads, and melting at 103 — 104° . The corresponding α -amidoxylcaproic acid,



forms vitreous prisms, and melts with decomposition at 151° . The α -isonitrosoisobutylacetamide, $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_2$, obtained by the action of sulphuric acid on the nitrile, separates in well developed tablets, and melts at 146 — 147° , the corresponding acid melting at 159 — 160° . CEnanthaldoxime forms α -amidoxylcaprylonitrile, $\text{C}_8\text{H}_{16}\text{N}_2\text{O}$, which is a white, paper-like mass, and melts at 92 — 93° . α -Amidoxylcaprylic acid itself crystallises in colourless rhombohedra, melts at 168° , and has strong reducing properties. α -Isonitrosocaprylamide, prepared

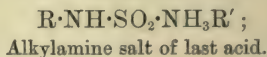
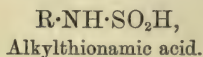
from sulphuric acid and the nitrile, separates from water in vitreous needles, and melts at 138—139°.

H. G. C.

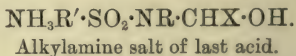
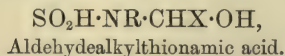
Thionylamines. By A. MICHAELIS (*Annalen*, **274**, 173—186; compare Abstr., 1891, 310 and 715).—Introductory and general remarks (see next abstract and this vol., i, 515). Primary aliphatic amines are converted into thionylamines on treatment in ethereal solution with thionyl chloride. The thionylamines are also formed by the interaction of the aliphatic amines and thionylaniline.

Aromatic amines containing the substituents Cl, Br, I, F, NO₂, OR, and COOR (R being an alkyl) yield thionylamines when dissolved in benzene and treated with thionyl chloride; those containing the substituents OH and COOH do not yield thionylamines.

The compounds obtained by the interaction of water and the thionylamines are thus represented by the author:—



whilst those obtained by the interaction of aldehydes and thionylamines are represented thus:—



Thionyl chloride is prepared either by the action of sulphurous anhydride on phosphoric chloride (Schiff) or by that of sulphuric anhydride on sulphur dichloride. The last method, when carefully carried out, yields 80 per cent. of the theoretical quantity of thionyl chloride, and the materials are much cheaper than those employed in the first-mentioned method; it, however, necessitates greater attention.

A. R. L.

Thionylamines of the Aliphatic Series. By A. MICHAELIS and O. STORBECK (*Annalen*, **274**, 187—196).—*Thionylmethylaniline*. SO:NMe, is prepared by adding methylamine to a cooled solution of thionylaniline in dry toluene, and allowing the mixture to remain some time at the ordinary temperature. It is a colourless or faintly yellow fuming liquid having an odour recalling that of bleaching powder, boils at 58—59°, and decomposes into methylamine and sulphurous anhydride when shaken with water. The yield is small, and besides aniline, a solid amorphous bye-product is also formed. Thionylethylamine (Abstr., 1891, 718) may be prepared in a similar manner.

Thionylpropylamine, SO:NPr, is obtained by the action of thionyl chloride on an ethereal solution of propylamine. It boils at 104°, and resembles its lower homologue, but is more stable towards water.

Thionylisobutylamine, SO:N·CH₂·CHMe₂, prepared in a similar manner to the last-named compound, is a colourless liquid having a penetrating, sweetish odour; it exerts a corrosive action on the skin, boils at 116°, and is decomposed by water.

Thionylamylamine, SO:N·C₅H₁₁, is a liquid having a less penetrating

odour than the analogues already described; it decomposes when distilled at the ordinary pressure, and, when shaken with water, boils at 90° under a pressure of 65 mm., and at 80° under a pressure of 45 mm.

Ethylthionamic acid ("ethylamine sulphite"), $\text{NH}_2\text{Et}\cdot\text{SO}_2$ ($\text{NHEt}\cdot\text{SO}_2\text{H}$?), separates as a white, hygroscopic powder when dry sulphurous anhydride is led into an ethereal solution of ethylamine. The corresponding propylamine and isobutylamine derivatives were also prepared. The isobutylamine compound loses sulphurous anhydride on remaining in the desiccator and furnishes *isobutylamine isobutylthionamate*, $2\text{NH}_2\cdot\text{C}_4\text{H}_9\cdot\text{SO}_2$, probably $\text{C}_4\text{H}_9\cdot\text{NH}\cdot\text{SO}_2\cdot\text{NH}_3\cdot\text{C}_4\text{H}_9$. *Amylthionamic acid* behaves in an analogous manner.

Benzaldehydepropylthionamic acid, $\text{NH}_2\text{Pr}^a\cdot\text{SO}_2\cdot\text{PhCHO}$, probably $= \text{SO}_2\text{H}\cdot\text{NPr}^a\cdot\text{CHPh}\cdot\text{OH}$, separates in white crystals on addition of benzaldehyde to an alcoholic solution of thionylpropylamine or of propylthionamic acid. It melts at 96° , its aqueous solution has an acid reaction, and on boiling it the compound is decomposed. When aniline is added to its aqueous solution, a compound having probably the constitution $\text{NH}_3\text{Ph}\cdot\text{SO}_2\cdot\text{NPr}^a\cdot\text{CHPh}\cdot\text{OH}$, is precipitated in crystals; it melts at 145° , and is decomposed by mineral acids with the evolution of sulphurous anhydride.

Benzaldehydeisobutylthionamic acid, $\text{NH}_2\cdot\text{C}_4\text{H}_9\cdot\text{SO}_2\cdot\text{PhCOH}$, melts at 116 — 117° , and, when treated with aniline, yields the compound $\text{C}_{17}\text{H}_{24}\text{N}_2\text{SO}_3$, melting at 160° .

Benzaldehydeamylthionamic acid, $\text{NH}_2\cdot\text{C}_5\text{H}_{11}\cdot\text{SO}_2\cdot\text{PhCOH}$, melts at 113° , and, on treatment with aniline, gives the compound $\text{C}_{18}\text{H}_{26}\text{N}_2\text{SO}_3$, melting at 138° .
A. R. L.

Syntheses with Aluminium Chloride. By P. GENVRESSE (*Compt. rend.*, 116, 1065—1067).—When 500 grams of normal propyl bromide is added gradually to a boiling mixture of 700 grams of benzene free from thiophen and 40 grams of aluminium chloride, and the product is washed with water, dried over calcium chloride, and fractionated, a mixture of normal propylbenzene and isopropylbenzene is obtained. It would seem that the proportion of the latter would be reduced by the use of as small a proportion of aluminium chloride as possible.
C. H. B.

Iodoso- and Iodoxy-compounds. By C. WILLGERODT (*Ber.*, 26, 1307—1313; see also this vol., i, 149).—Iodosobenzene, when boiled with water, either in the presence or absence of air, is converted into iodoxybenzene and iodobenzene. When iodosobenzene is treated with an aqueous solution of potassium iodide, only a partial decomposition takes place. In the presence of acetic or hydrochloric acid, however, the reaction is quantitative and iodine is liberated. The titration of this solution with sodium thiosulphate gives a greater quantity of oxygen than that required by theory, indicating the presence of iodoxybenzene in the iodosobenzene.

Phenyl iodochromate, $\text{C}_6\text{H}_5\cdot\text{I}\cdot\text{CrO}_4$, is obtained by adding chromic acid to an acetic acid solution of iodosobenzene. It is a yellow compound which reddens on drying, explodes at 66 — 67° , and liberates

the theoretical quantity of iodine from a solution of potassium iodide containing sulphuric acid.

The nitrate, $\text{IPh}(\text{NO}_3)_2$, has been obtained in thick, yellow tablets belonging to the monoclinic system; $a : b : c = 2.3124 : 1 : 1.2784$, $\beta = 51^\circ 45'$.

Iodoxybenzene, $\text{C}_6\text{H}_5\cdot\text{IO}_2$, when treated with hydrochloric acid in aqueous solution, is converted into iodosobenzene hydrochloride, and chlorine is evolved. When treated with hydrogen peroxide, it is converted into iodobenzene, and oxygen is liberated. With chromic acid in aqueous solution, it yields iodobenzene; in acetic acid solution, however, it yields a yellow compound which explodes at 73° .

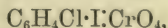
Metanitriodobenzene dichloride, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{ICl}_2$, is obtained by treating a cold chloroform solution of metanitriodobenzene with chlorine. It crystallises in large, yellow plates or prisms, decomposes at $100\text{--}102^\circ$, and decomposes when dissolved in acetic acid or alcohol, whereby the alcohol is converted into aldehyde.

Metanitriodosobenzene, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{IO}$, is obtained by the action of dilute sodium hydroxide on the preceding compound. It sinters at 180° and decomposes at $190\text{--}195^\circ$. The *acetate*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{I}(\text{OAc})_2$, crystallises in almost colourless prisms, and melts without decomposition at $150\text{--}155^\circ$. The *chromate* is a red, microcrystalline powder, and explodes at 95° .

Metanitriodoxybenzene, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{IO}_2$, is obtained together with nitriodobenzene by boiling the iodoso-compound with water. It crystallises in colourless lamellæ, and explodes at 215° .

E. C. R.

Orthiodosobenzene and Orthochloriodoxybenzene. By C. WILLGERODT (*Ber.*, 26, 1532—1534).—When a well-cooled solution of orthiodobenzene is treated with chlorine, *ortho-chlorophenyl iodo-chloride*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{ICl}_2$, separates as a pale yellow, crystalline powder, which decomposes with violent evolution of gas at $95\text{--}98^\circ$, and quickly darkens on exposure to air and light. On treatment with dilute soda, it is converted into *ortho-chloriiodosobenzene*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{IO}$, which separates out as a very pale yellow powder, and cannot be re-crystallised from any solvent. It explodes without any report at $83\text{--}85^\circ$, and on treatment with acetic acid yields the *diacetate*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{I}(\text{OAc})_2$, which crystallises in colourless, transparent prisms, becomes plastic at 125° , and melts at 140° . The *chromate*,



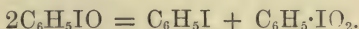
is a brownish-red powder which decomposes at $56\text{--}57^\circ$ with a slight report.

When orthochloriiodosobenzene is boiled with water, orthochloriiodobenzene distils over, and the hot solution on cooling deposits *ortho-chloriiodoxybenzene*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{IO}_2$, in small, white needles, which decompose with a sharp report at 203° . It also yields a *chromate* on treatment with acetic acid and chromic acid solutions.

H. G. C.

Iodoso-compounds. By P. ASKENASY and V. MEYER (*Ber.*, 26, 1354—1370; compare *Abstr.*, 1892, 1460).—Some of the properties

assigned by Willgerodt (this vol., i, 149) to iodosobenzene differ so much from those observed by Meyer and Wachter for iodosobenzoic acid that the authors have repeated Willgerodt's experiments, and have obtained different results. Thus they find that iodosobenzene liberates quantitatively 2 atoms, and iodoxybenzene 4 atoms, of iodine from potassium iodide, whereas Willgerodt found that the former set free approximately 1 atom of iodine, and the latter had no action on the iodide. This difference is probably partly due to the fact that Willgerodt did not acidify the potassium iodide solution with acetic acid. They are also unable to confirm Willgerodt's statement that iodosobenzene is converted into iodoxybenzene by the action of the oxygen of the air; the latter, in reality, takes no part in the reaction, but the iodobenzene on heating is converted into iodobenzene and iodoxybenzene:



The explosion of iodosobenzene observed by Willgerodt is in reality due to the iodoxybenzene which is formed when it is heated.

Owing to the different melting points of the various specimens of iodosobenzoic acid, the authors thought it possible that a mixture of two isomeric acids might be present, but all yield the same crystalline acetyl derivative, and must therefore be identical.

Iodosobenzoic acid may be prepared from pure orthiodobenzoic acid either by the action of fuming nitric acid or of acid potassium permanganate, and also by acting on it with chlorine in chloroform solution and treating the dichloride with alkalis. The colourless acid dissolves in alkalis and sodium carbonate solution, forming deep yellow solutions which are reprecipitated by mineral acids. Its conductivity has been found by Ostwald to be $k = 0.00006$, and it is, therefore, one of the feeblest known acids. The *sodium* and *calcium* salts are amorphous, and the *silver* salt forms a yellow precipitate which is very explosive when dry; no ethereal salts could be prepared.

On aromatic amido-compounds, iodosobenzoic acid acts as an oxidising agent yielding amorphous colouring matters, and with ethylamine, it forms salicylic acid. When treated with potassium permanganate in alkaline solution, it is partially reduced to form iodobenzoic acid, and partially oxidised to iodic acid and iodoxybenzoic acid; the latter compound will be described later. Boiling aqueous alkalis attack the acid very slightly with formation of a small quantity of iodate, but with alcoholic soda, it yields salicylic acid, the oxygen simultaneously evolved acting on the alcohol with formation of aldehyde.

In order to decide if possible between the two possible formulæ, $\text{IO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ and $\text{C}_6\text{H}_4\text{--}\begin{smallmatrix} \text{I}(\text{OH}) \\ \text{CO} \end{smallmatrix}\text{--}\text{O}$, the authors treated iodosobenzoic acid with acetic anhydride, and obtained an *acetyl* derivative, $\text{C}_7\text{H}_4\text{O}_3\text{IAc}$, crystallising in apparently monosymmetric prisms, and melting at $166\text{--}167^\circ$. The formation of an acetyl compound appeared to support the second of the above formulæ, as no case has been hitherto observed in which, by the direct action of acetic an-

hydride, the hydrogen of the carboxyl group is displaced by the acetyl group. It was found, however, on further investigation that paradimethylamidobenzoic acid also yields an acetyl derivative under similar conditions, and therefore no conclusions as to the constitution of iodosobenzoic acid can be drawn from this reaction. The acetyl compound of the dimethylamidobenzoic acid, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{COOAc}$, crystallises in needles, and melts at 109° .

All attempts to obtain iodoso-derivatives from meta- and para-iodobenzoic acid have been without success. Of the two iodoparatoluic acids, the one in which the iodine atom occupies the ortho-position to the carboxyl group yields an iodoso-derivative similar to iodosobenzoic acid, but the isomeric acid does not yield a corresponding compound. If, however, pariodobenzoic acid be previously nitrated, it may be converted by the further action of fuming nitric acid into an iodoso-derivative, $\text{IO}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{COOH}$, which is an intensely yellow substance, insoluble in the usual solvents. When treated with alcoholic soda, it is converted into sodium iodate, sodium nitrobenzoate, and sodium nitriodobenzoate. In a similar manner the iodoparatoluic acid, which does not yield an iodoso-compound directly, may be made to do so by previous nitration.

H. G. C.

Metallic Compounds of the Benzene Series. By G. PERRIER (*Compt. rend.*, 116, 1140—1143).—When phenylic benzoate, resorcinol or quinol dibenzoate, or phenylic phthalate is boiled with aluminium chloride and carbon bisulphide, a crystalline compound, almost insoluble in carbon bisulphide, separates on cooling. Phenylic benzoate yields colourless crystals of the compound $(\text{C}_6\text{H}_5\cdot\text{COOPh})_2\cdot\text{Al}_2\text{Cl}_6$, which dissociates somewhat rapidly when exposed to air, and is at once split up into its constituents by water. Resorcinol and quinol dibenzoates yield compounds of the formula $2\text{C}_6\text{H}_4(\text{OBz})_2\cdot\text{Al}_2\text{Cl}_6$. The same compounds are formed when the chlorides of the acids of the benzene series are heated with the phenols in presence of carbon bisulphide and aluminium chloride.

Under the latter conditions, β -naphthol yields golden-yellow crystals of the composition $2\text{OBz}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}\cdot\text{Al}_2\text{Cl}_6$. It dissociates slightly when exposed to air, and, when treated with water, it yields aluminium chloride and a benzoynaphthol. The latter crystallises from ether-alcohol in pale yellow, silky needles which melt at 141° , and sublime easily. It dissolves in alkalis, and is reprecipitated by acids. Its sodium salt crystallises in orange plates, and the ammonium salt in yellow needles. Benzoynaphthol combines with phenylhydrazine.

Other naphthols behave in the same way. Chlorides of the acids of the acetic series likewise yield ketonic phenols when boiled with naphthols in presence of aluminium chloride, and the same reaction takes place even when the phenol has only one nucleus; whereas, under the same circumstances, chlorides of the acids of the benzene series yield only ethereal salts.

Phenol combines with aluminium chloride to form large, colourless lamellæ; thymol yields rose-white crystals, very unstable when exposed to air; and β -naphthol yields a greenish-yellow, crystalline

powder. All these products, when treated with water, split up into aluminium chloride and the original phenol.

Ferric chloride behaves in the same way, but the results are less distinct.

C. H. B.

Action of Formaldehyde on Nitrosodimethylaniline. By J. PINNOW and G. PISTOR (*Ber.*, 26, 1313—1315).—When finely-powdered nitrosodimethylaniline is heated with formaldehyde on the water-bath, a violent reaction takes place, and the product, when precipitated with water, yields tetramethyldiamidoazoxybenzene, $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, which melts at 243° (uncorr.), and yields paramidodimethylaniline when boiled with tin and hydrochloric acid, and tetramethyldiamidoazobenzene when boiled with alcoholic potash and zinc dust.

The mother liquors of the preceding compound contain the *formyl* derivative of *paramidodimethylaniline*, $\text{HCO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, which is separated by fractional precipitation with salt. It crystallises in silvery leaflets, melts at 108° , and, when boiled with hydrochloric acid or alkalis, yields formic acid and paramidodimethylaniline. The *picrate* melts at 188° . The *mercurochloride* melts at 171° .

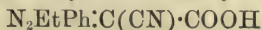
E. C. R.

Action of Phenylhydrazine on Diazobenzene. By A. WOHL (*Ber.*, 26, 1587—1589).—In view of the recent paper of Curtius (this vol., i, 463), the author gives an account of the investigation he has made on the action of phenylhydrazine on diazobenzene, although this is at present incomplete.

If phenylhydrazine acetate and diazobenzene acetate are allowed to interact in dilute acetic acid solution, a precipitate is formed, which may be purified by crystallising from ether and washing with alcohol, and then forms pale yellow crystals melting at 71° with decomposition. It explodes when touched with a warm glass rod, and, on warming in alcoholic solution, gives off nitrogen, the odour of phenylhydrazine being also perceptible. It appears to have the formula $\text{C}_{12}\text{H}_{12}\text{N}_4$, and is probably formed directly from phenylhydrazine and diazobenzene with elimination of water.

H. G. C.

Ethylic Azobenzenecyanacetate. By F. KRÜCKEBERG (*J. pr. Chem.* [2], 47, 591—592).—The two modifications of this compound melt at 125° (α -) and at 82° (β -) respectively; the substance which melts at 106 — 108° (this vol., i, 210) is probably a molecular mixture of the two. Both modifications are optically inactive. The benzoyl derivative (*loc. cit.*) is hydrolysed by potash to potassium ethylic azobenzeneacetate; the ethyl derivative (*loc. cit.*) under the same treatment yields a salt of ethylazobenzenecyanacetic acid,



(m. p. 147°). The reaction between ethylic chlorocarbonate and potassium ethylic azobenzenecyanacetate yields the carboxethyl derivative, $\text{COOEt}\cdot\text{N}_2\text{Ph}\cdot\text{C}(\text{CN})\cdot\text{COOEt}$.

The compounds obtained by the action of ortho- and of para-diazotoluene chloride, respectively, on ethylic cyanacetate also occur each in two forms: ethylic α -azorthotoluenecyanacetate melts at 85° , the

β -derivative at 133° ; ethylic α -azoparatoluenecyanacetate melts at 118° , the β -derivative at 74° .

The study of the action of nitrous acid on these substances is not yet complete.

A. G. B.

Stereoisomerism of the Benzhydroxamic acids. By A. WERNER (*Ber.*, 26, 1561—1567; compare Abstr., 1892, 461).—This paper consists chiefly of a defence of the author's nomenclature and results against Lossen's criticisms (Abstr., 1892, 711). He has repeated the portion of his work referring to the determination of the stereometric formulæ of the two ethylbenzhydroximic acids, and has confirmed his previous results in all respects but one, namely, the formula of the phosphate of the "anti-" acid. This was first given as $\text{PO}(\text{O}\cdot\text{N}\cdot\text{CPh}\cdot\text{OEt})_3 + \text{H}_2\text{O}$, but it is now found that the substance is anhydrous.

In his first experiments, the author was unable to obtain the benzoyl derivative of ethylsynbenzhydroximic acid, as by the action of benzoic chloride and soda, the acid is converted into the "anti-" benzoyl compound. If, however, the soda be replaced by potash, the "syn-" derivative may readily be obtained, and, after crystallisation from ether, melts at 58° .

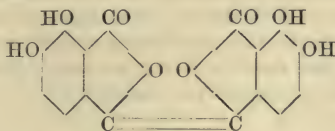
H. G. C.

Constitution of Gallic Blue or Tannin-indigo. By P. CAZENEUVE (*Compt. rend.*, 116, 884—887).—When nitrosodimethylaniline is heated with gallanilide in presence of acetic acid, alcohol, or other solvent, it yields a brilliant olive-green colouring matter, insoluble in water or in alkalis, but soluble in aniline, from which it can be crystallised. This compound dissolves in concentrated sulphuric acid, forming a blue-violet solution, and, on addition of water, a deep violet precipitate is obtained. When 5 parts of this olive-green product is heated with 20 parts of alcohol and 20 parts of a 40 per cent. solution of sodium hydrogen sulphite, a soluble sodium salt of a sulphonic derivative is obtained. The sulphonic acid can also be formed by the direct action of sulphuric acid. The sodium salt has the composition $\text{NaSO}_3\cdot\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_4\text{Cl}$. The relation of the sulphonic derivative and the insoluble green compound to gallocyanine is shown by graphic formulæ. Gallocyanine is an oxindophenol, and gallic blue is derived from it by the substitution of $\text{NH}\cdot\text{C}_6\text{H}_5$ for an oxygen atom in the carboxyl group.

C. H. B.

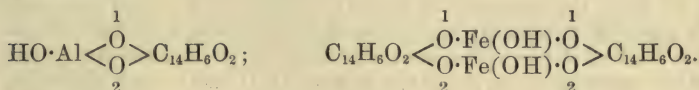
The Theory of the Formation of Coloured Compounds with Mordants. By C. LIEBERMANN (*Ber.*, 26, 1574—1578).—The author has shown, in conjunction with Bistrzycki (this vol., i, 371), that numerous derivatives of opianic acid are coloured, and also that certain of them, such as tetramethoxydiphthalyl and bisdimethoxymetaindolone, on treatment with concentrated sulphuric acid, yield colouring matters which unite with mordants, forming coloured lakes. The action of sulphuric acid consists in the elimination of the methyl groups, and the same reaction may be brought about by heating with concentrated hydriodic acid. Tetramethoxydiphthalyl is thus converted into the corresponding tetrahydroxydiphthalyl, which has been

previously investigated by Goldschmiedt and Egger (Abstr., 1891, 1371), who have conclusively shown that its constitution is represented by the formula



Each pair of hydroxyl groups occupies the ortho-position, thus again confirming the supposition of the author and Kostanecki (Abstr., 1888, 274; 1889, 868) that, with the phenol and acid colouring matters, only those compounds containing at least two hydroxyl groups in the ortho-position yield coloured derivatives with mordants.

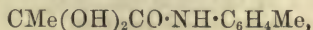
Hitherto no explanation has been given of this property, and the author suggests that the reason is to be found in the fact that only in this case is the hydrogen of both hydroxyl groups capable of combining with the hydroxyl groups attached to one and the same metallic atom (such as Al) or with hydroxyl groups attached to a double atom (such as Fe·Fe). Alizarin red and violet would then have the following formulæ:—



This property of the orthohydroxy-compounds would be in strict accordance with their general behaviour, inasmuch as they so frequently undergo condensation with formation of ring derivatives. The fact that the properties of the metal are often masked in the coloured derivatives would be also then explained, as this frequently occurs when the metal is present in the molecule in a closed chain of atoms.

H. G. C.

Some Anilides and Toluidides which exist in two Modifications. By C. A. BISCHOFF and P. WALDEN (*Ber.*, 26, 1461—1462).—By the action of phosphoric chloride on compounds of the type $\text{OH} \cdot \text{CHX} \cdot \text{CO} \cdot \text{NH} \cdot \text{Y}$ [X = an aliphatic alkyl; Y = an aromatic alkyl], chloro-derivatives are obtained which, when treated with water, lose chlorine, and pass into substances $\text{XCO} \cdot \text{CO} \cdot \text{NH} \cdot \text{Y}$ or, as they are soluble in alkali, $\text{XCO} \cdot \text{C}(\text{OH}) \cdot \text{NH} \cdot \text{Y}$ (compare Nef, Abstr., 1892, 1440). When the alkaline solutions of these compounds are acidified, polymeric substances of higher melting point and twice as great molecular weight are precipitated. The following compounds have been obtained up to the present, $\text{X} = \text{CH}_3$:—*Pyruvic anilide* melts at 104° , and yields a *polymeride* melting at 196° ; *pyruvic orthotoluidide* melts at 71° , and yields a *polymeride* melting at 174° ; *pyruvic paratoluidide* melts at 109° , and yields a *polymeride* melting at 201° . $\text{X} = \text{C}_2\text{H}_5$:—The *paratoluidide* melts at 131° , and yields a *polymeride* melting at 192° . Two new hydrazide *pyruvic orthotoluidides*,



insoluble in aqueous alkali, exhibit the same relation. A modification melting at 111° is formed when the chlorinated intermediate product is distilled under diminished pressure and decomposed with water; whilst, when the chloro-derivative is decomposed directly with water, a compound having twice the molecular weight and melting at 177° is obtained; these two modifications are not interconvertible. Nef promises to further investigate the matter. A. R. L.

Condensation of Acetophenone on heating alone or with Zinc Chloride. By C. ENGLER and L. DENGLER (*Ber.*, 26, 1444—1449; compare Delacre, *Abstr.*, 1892, 993).—When acetophenone is boiled in a reflux apparatus for 16 days, 20 per cent. of unaltered substance passes over on distillation, and the residue consists of 20 per cent. of dyprone, 45 per cent. of triphenylbenzene, and a small quantity of a compound melting at 109° . The latter proves to be

$\alpha\beta'$ -diphenylfurfuran, $\begin{array}{c} \text{CPh}\cdot\text{CH} \\ | \\ \text{CH}\cdot\text{CPh} \end{array} > \text{O}$, and may be prepared by heating dyprone with nitrobenzene at 190° . It forms white leaflets, having a bluish fluorescence; its solutions also exhibit fluorescence. By heating acetophenone in a sealed tube at temperatures varying from 290° to 370° , the compounds already mentioned are produced together with gaseous products; the amount of dyprone obtained decreases, whilst that of triphenylbenzene increases, as the temperature rises.

When acetophenone is heated at 130 — 170° with zinc chloride, the products are dyprone and triphenylbenzene, but no diphenylfurfuran; at higher temperatures benzoic acid is also formed, apparently through the presence of zinc oxychloride. A. R. L.

Behaviour of Organic Acids and Ethereal Salts at High Temperatures. By C. ENGLER and E. LÖW (*Ber.*, 26, 1436—1443).—In continuation of previous work on the formation of mineral oil (*Abstr.*, 1888, 928; 1889, 586), the authors describe experiments having for their object the explanation of the occurrence of aromatic hydrocarbons in the mineral oil. Some experiments were carried out in a sealed tube bent at an obtuse angle; one part of the tube was heated in a furnace, the other portion projecting downwards beyond the furnace, so that distillation proceeded at a high pressure from the hot to the cold portion of the tube. Other experiments were made in a sealed tube heated in the usual manner. The pressure was approximately measured by means of small capillary tubes, closed at one end, the compression of the inclosed air being measured by the movement of a globule of mercury. The gaseous products were removed from time to time when the pressure was excessive.

When phenylacetic acid is heated in an ordinary sealed tube at 355 — 375° , toluene, carbonic anhydride, dibenzyl ketone, and a small quantity of carbonic oxide are formed. By heating the acid at 375° in an exhausted vessel in so small a quantity that no excess of pressure is produced, the same decomposition occurs, so that pressure has no direct influence on the reaction. It is noteworthy that phenylacetic acid is a normal decomposition product of putrefactive

proteïds, and the presence of benzenoid hydrocarbons in mineral oil may not therefore be exclusively due to a pyrogenetic process.

Benzoic and acetic acids undergo slight decomposition only when heated at 390° ; cinnamic acid is partially decomposed at 320° . Ethylic acetate is unaltered at 290° ; methylic phenylacetate decomposes at 360° into toluene, methyl alcohol, and gaseous products; methylic benzoate undergoes very little decomposition at $380\text{--}400^{\circ}$, but ethylic benzoate is decomposed at 360° into benzoic acid and ethylene, and the amylic salt at $340\text{--}350^{\circ}$ into benzoic acid and amylene.

The authors believe that their experiments show that the acids decompose the more readily the more negative the nature of their non-carboxylic residues. The tendency of the hydrogen of the carboxyl group to combine with methyl in acetic acid is much less than it is to combine with the group CH_2Ph in phenylacetic acid.

A. R. L.

New Synthesis of Allocinnamic acid. By C. LIEBERMANN (*Ber.*, 26, 1571—1574).—Claisen and Crismer have shown that when benzalmalonic acid, $\text{CHPh}\cdot\text{C}(\text{COOH})_2$, is heated at about 195° , it splits up into carbonic anhydride and cinnamic acid. The author has repeated the experiment, heating the acid in quantities of 20—25 grams in an oil bath at 195° for 6—9 minutes, and finds that under these conditions about 5—6 per cent. of the benzalmalonic acid is converted into allocinnamic acid, the remainder being converted into cinnamic acid.

Benzalmalonic acid has in all probability the stereometric formula $\text{Ph}\cdot\text{C}\cdot\text{H}$
 $\text{COOH}\cdot\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot\text{COOH}$, and the formation of allocinnamic acid in this manner is therefore an additional proof of the supposition that the two acids are stereoisomerides.

H. G. C.

Condensation of Cinnamic acid with Hydrocarbons. By W. KARSTEN (*Ber.*, 26, 1579—1583).—Cinnamic acid undergoes condensation with toluene and metaxylene in presence of sulphuric acid in the same manner as with benzene (*Abstr.*, 1891, 1484; 1892, 848, 1228), forming phenyltolylpropionic and phenylxylylpropionic acids. *Phenyltolylpropionic acid*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COOH}$, is a light, white powder insoluble in water, and melts at $145\text{--}146^{\circ}$; its *calcium* salt forms microscopic, white plates, and its *silver* salt a white precipitate susceptible to light, whilst the *methylic* salt is an oil. When treated with permanganate in alkaline solution, the acid is converted into phenyl paratolyl ketone, $\text{COPh}\cdot\text{C}_6\text{H}_4\text{Me}$, and parabenzoylbenzoic acid, the formation of this ketone proving that the original acid is β -phenyl- β -paratolylpropionic acid.

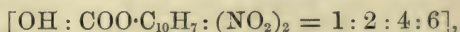
Phenylxylylpropionic acid, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COOH}$, is a crystalline precipitate; it melts at $111\text{--}112^{\circ}$, and yields *calcium* and *silver* salts having the formulæ $(\text{C}_{17}\text{H}_{17}\text{O}_2)_2\text{Ca}$ and $\text{C}_{17}\text{H}_{17}\text{O}_2\text{Ag}$ respectively. On oxidation, it does not give a ketone, but, according to the length of time allowed for the oxidation, yields compounds in which one or both of the methyl groups are oxidised to carboxyl. The first compound, *phenylcarboxytolylpropionic acid*,



is a white, crystalline powder, and melts at 252° ; the *silver* salt is a white, flocculent precipitate somewhat susceptible to light. *Phenyldicarboxyphenylpropionic acid*, $C_6H_5(COOH)_2 \cdot CHPh \cdot CH_2 \cdot COOH$, may be crystallised from hot water, and melts at 218° with decomposition; it forms *calcium* and *barium* salts having the formulæ $(C_{17}H_{11}O_6)_2Ca_3$ and $(C_{17}H_{11}O_6)_2Ba_3$.
H. G. C.

Phenylic and α - and β -Naphthylic Salicylates. By H. ECKENROTH and M. WOLF (*Ber.*, 26, 1463—1470).—*Phenylic dibromosalicylate* $[OH : COOPh : Br_2 = 1 : 2 : 4 : 6]$ is obtained, together with the *monobromo*-derivative (m. p. 98°), when bromine is added to an alcoholic solution of phenylic salicylate in the cold; at a higher temperature, in presence of excess of bromine, the dibromo-derivative alone is formed. It crystallises in white, silky needles, melts at 128° (uncorr.), and yields dibromosalicylic acid (m. p. 219°) on hydrolysis with soda. *α -Naphthylic dibromosalicylate* melts at 155° , and the *β -naphthylic* derivative melts at 191° .

α -Naphthylic nitrosalicylate $[OH : COO \cdot C_{10}H_7 : NO_2 = 1 : 2 : 4]$ is obtained, together with the *dinitro*-derivative



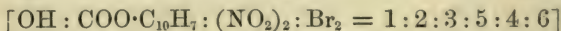
by nitrating a dilute solution of *α -naphthylic salicylate* in glacial acetic acid at 0° . The *dinitro*-compound, which melts at 192° , separates in yellow leaflets, whilst the *mononitro*-compound remains in the mother liquor. The corresponding *β -naphthylic* derivatives are obtained in the same manner. The *mononitro*-compound melts at 201° , and the *dinitro*-compound melts at 254° .

Phenylic salicylate phenylcarbamate, $NHPh \cdot CO \cdot O \cdot C_6H_4 \cdot COOPh$, is obtained by heating phenylic salicylate with phenylic cyanate in a sealed tube at 160° , or, better, by heating carbanilide with phenylic salicylate in a reflux apparatus; it melts at 241 — 242° . The corresponding *α -naphthylic* compound melts at 244° , and the *β -naphthylic* derivative melts at 268° .

Phenylic acetylsalicylate, $OAc \cdot C_6H_4 \cdot COOPh$, is obtained by heating phenylic salicylate with acetic anhydride in a reflux apparatus; it melts at 98° . The *α -naphthylic* compound melts at 91° , and the *β -naphthylic* compound melts at 136° .

When phenylic or the naphthylic salicylates are heated with alcoholic ammonia in a sealed tube at 100° , salicylamide is formed.

β -Naphthylic dinitrodibromosalicylate



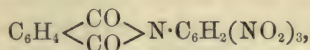
was prepared by adding the calculated amount of nitric acid to a boiling solution of the dibromo-compound in glacial acetic acid. The product crystallised in reddish needles, melted between 248° and 262° , and was not obtained pure. It is sparingly soluble in all solvents. *Dinitrodibromosalicylic acid* obtained on hydrolysis forms yellowish needles, and melts at 162° .

Clemm (*Ber.*, 3, 126) has shown that a chlorine atom in a contiguous position to a nitro-group is readily replaced by other radicles. When the above-described *β -naphthylic dinitrodibromo*-

salicylate is heated with aniline and a little alcohol in a reflux apparatus, the compound $\text{NPh}\cdot\text{C}_6\text{Br}(\text{NO}_2)_2(\text{OH})\cdot\text{COO}\cdot\text{C}_{10}\text{H}_7$ is obtained. It crystallises in brown, lustrous needles, and melts at 222° . Attempts to replace the second bromine atom were unsuccessful.

A. R. L.

Action of Phthalic Chloride on Trinitraniline. By H. A. ROUFFAER (*Rec. Trav. Chim.*, **11**, 275—277).—By heating these two substances together at 160° , *trinitrophenylphthalimide*,



is obtained in monoclinic crystals melting at 251° .

C. F. B.

Action of Thionyl Chloride on Benzylamine. By A. MICHAELIS and O. STORBECK (*Annalen*, **274**, 197—200; see this vol., i, 504).—Benzylamine does not yield a thionylamine when treated in ethereal solution with thionyl chloride, but the products of the reaction are benzylamine hydrochloride, benzaldehyde, and a compound containing sulphur. By the action of thionylaniline on benzylamine, there is formed benzilidenaniline, which results from the combination of the primary products benzaldehyde and aniline. A compound was also isolated giving numbers on analysis intermediate between those required for ammonium thiosulphate and ammonium trithionate.

A. R. L.

Thionylamines of the Aromatic Series. By A. MICHAELIS and others (*Annalen*, **274**, 200—266; see this vol., i, 504).—The sp. gr. of thionylaniline at 15° is 1.2360. The compound yields aniline and hydrogen sulphide or sulphur, on reduction with zinc-dust and acetic acid. When chlorine is passed into a solution of thionylaniline in light petroleum, trichloraniline (m. p. 78°) is formed; the action of chlorine is therefore analogous to that of bromine (*Abstr.*, 1891, 716). A solution of *chlorothionylaniline*, $\text{NPh}\cdot\text{SCl}_2$, appears to be formed when thionylaniline is dissolved in carbon tetrachloride, and the solution heated with phosphoric chloride; the compound cannot be isolated, as it decomposes in contact with moisture into thionylaniline, or in contact with hydrogen chloride into parachloraniline hydrochloride. Azobenzene is obtained by the action of thionylaniline on an ethereal solution of hydrazobenzene. When thionylaniline is heated with aniline in a sealed tube at 200° , the chief product is a dark-blue powder having a coppery shimmer; it is almost insoluble in alcohol, and may have the constitution $\text{NH} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{S}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$, and is, perhaps, identical with the colouring matter obtained by Bennert (*Chem. Centr.*, 1889, 656) by the action of sulphuric anhydride on aniline. Similar substances are obtained by heating diphenylaniline and methylaniline with thionylaniline.

When thionylaniline (1 mol.) is heated with dimethylaniline (2 mols.) and some zinc chloride, *thiodimethylaniline*, $\text{S}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, melting at 125° , is obtained, together with a *tetramethylphenyltri-amidotriphenylmethane*, probably $\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, which crystallises from alcohol in nacreous leaflets, and melts at 176° ; the

picrate melts at 185°. The colour *base* obtained on oxidation has all the properties of methyl violet.

Thionylmetachloraniline (*loc. cit.*) melts at 4°, and when dissolved in alcohol, together with metachloraniline and benzaldehyde, the compound $2C_6H_4Cl \cdot NH_2 \cdot SO_2 \cdot PhCHO$ separates with the development of heat; it forms white needles, and melts at 108°.

Thionylorthochloraniline boils at 207° (46 mm.), solidifies at -8°, is decomposed by water, and gives a *condensation derivative* with benzaldehyde.

Thionylparabromaniline crystallises from light petroleum in lustrous, yellow tables having an aromatic odour, and melts at 60—61°. Thionylmetabromaniline melts at 32°; and thionylorthobromaniline boils at 210° (46 mm.), and melts at 3—4°. Thionyltetrabromaniline, derived from Körner's tetrabromaniline (*Jahres.*, 1875, 343) forms yellow needles, and melts at 78°.

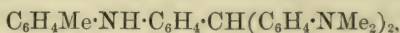
Thionyliodaniline crystallises in yellowish-brown tables, melts at 54°, and gives a *condensation derivative*, $2C_6H_4I \cdot NH_2 \cdot SO_2 \cdot PhCHO$, with benzaldehyde melting at 121—122°. Thionylmetadiodaniline melts at 74°, and its *condensation derivative* with benzaldehyde melts at 78°.

The *condensation derivative*, $2NO_2 \cdot C_6H_4 \cdot NH_2 \cdot SO_2 \cdot PhCHO$, derived from thionylmetanitraniline and benzaldehyde, forms small, yellow prisms, and melts at 90—91°. The corresponding *derivative* of thionylparanitraniline melts at 95—96°.

Thionylorthonitraniline forms small, yellow prisms, and melts at 52°; its *condensation derivative* with benzaldehyde melts at 88°.

The sp. gr. of thionylparatoluidine (*loc. cit.*) at 15° is 1.1685. Thionylmetatoluidine boils at 220°, and is more stable towards water than its isomeride. By heating thionylparatoluidine with aniline or diphenylamine at about 200°, *condensation products* are obtained.

Tetramethyltolyltriamidotriphenylmethane,



melting at 177°, is obtained by heating together at 80° thionylparatoluidine (1 mol.), dimethylaniline (2 mols.), and zinc chloride; the *picrate* melts at 184°.

Thionylmetabromoparatoluidine forms small, yellowish-brown crystals, and melts at 47°; it is stable towards water. Thionylmetabrom-orthotoluidine crystallises in long prisms, and melts at 50°.

Thionylorthonitroparatoluidine melts at 44°; thionylmetanitroparatoluidine melts at 38—39°, and is very readily decomposed by water.

Thionylxylidine [$Me_2 : NSO = 1 : 3 : 4$], boils at 238°, does not solidify at -15°, and its sp. gr. is 1.149 at 14°. It yields with benzaldehyde the *condensation derivative*, $2C_6H_5Me_2 \cdot NH_2 \cdot SO_2 \cdot PhCHO$, which melts at 98°, and on keeping is converted into xylidine sulphite and benzylidenexylidine, $C_6H_5Me_2 \cdot N \cdot CHPh$, an oil boiling above 300°. With anisaldehyde, a *compound* melting at 111° is obtained.

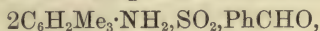
Thionylxylidine [$Me_2 : NSO = 1 : 2 : 4$] boils at 131° (20 mm.), and solidifies at -9°.

Thionylfluoro-xylidine [$Me_2 : F : NSO = 1 : 3 : 4 : ?$] is obtained

from a fluoro-xylidine which will be described in a subsequent paper; it boils at 142—144° (45 mm.).

Thionylxylidine [$\text{Me}_2 : \text{NSO} = 1 : 4 : 2$] boils at 119° (20 mm.), solidifies at -8° , and, when treated with benzaldehyde, yields the *benzylidenexylidine*, $\text{C}_6\text{H}_5\text{Me}_2\text{N}\cdot\text{CHPh}$, melting at 96° .

Thionyl- ψ -cumidine boils under the ordinary pressure at 246° , but not without decomposition, and under a pressure of 20 mm. at 129° ; it solidifies at -10° , is very stable towards water, and has a sp. gr. 1.078 at 14° . The *condensation product* with benzaldehyde,



melts at 108° , and an analogous *compound* with cinnamaldehyde melts at 68° .

Thionylcumidine, $\text{C}_6\text{H}_4\text{Pr}\cdot\text{N}\cdot\text{SO}$, boils at 156—158° (60 mm.), and can be boiled with water for a considerable time without undergoing decomposition.

Thionylmesidine, $\text{C}_6\text{H}_2\text{Me}_3\text{N}\cdot\text{SO}$, can be distilled in a current of steam without decomposition ensuing, boils at 241° with slight decomposition, has a sp. gr. 1.121 at 14° , and solidifies at -11° . The *condensation derivative* with benzaldehyde, $2\text{C}_6\text{H}_2\text{Me}_3\text{NH}_2\cdot\text{SO}_2\cdot\text{PhCHO}$, melts at 88° , and the corresponding *derivative* with anisaldehyde melts at 79.5° ; when an alcoholic solution of the latter is exposed to the air, *methoxybenzylidenemesidine*, melting at 67° , is formed.

Thionylnitromesidine, derived from Noelting's nitromesidine (Abstr., 1891, 693), crystallises in groups of small, yellow needles, melts at 77° , and is slowly decomposed by cold water. Dinitromesidine (*loc. cit.*) yields a *thionyl derivative*, melting at 127° .

Unsuccessful attempts were made to isolate pure thionyl derivatives of para- and ortho-amidophenol. *Benzaldehydphenolparathionamic acid*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{SO}_2\cdot\text{PhCHO}$, is prepared by saturating an alcoholic solution of paramidophenol with dry sulphurous anhydride, and adding the calculated quantity of benzaldehyde. It crystallises in colourless plates, and is insoluble in ether, but very soluble in water, and when heated loses the elements of sulphurous acid, and passes into benzylideneparamidophenol, $\text{CHPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$. It therefore shows the melting point, 183° , of the latter compound. *Anisaldehydphenolparathionamic acid* forms white crystals; it becomes yellow at 140° , and melts at 188° , being converted into methoxybenzylideneparamidophenol.

Orthothionylanisidine, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{SO}$, is an oil boiling at 203° (65 mm.). *Parathionylphenetidine*, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{SO}$, boils at 220° (200 mm.), and solidifies to yellow needles when cooled; it melts at 32° .

Thionyl chloride converts metamidobenzoic acid into the anhydride (Harbordt, *Annalen*, 123, 289); a thionyl derivative could not be prepared. *Ethyl metamidobenzoate* forms a *thionyl derivative*, $\text{SO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{COOEt}$, boiling at 195° (105 mm.); the corresponding *methylic derivative* boils at 212° (90—100 mm.), and melts at 57° .

Amidoazobenzene yields a *thionyl derivative*, $\text{SO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$, which crystallises in small, reddish-violet, lustrous needles, and melts at 113° ; it cannot be distilled, even under diminished pressure, without decomposition.

Thionyldiamidoazobenzene (*thionylchrysoiline*), $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{NSO})_2$, forms red needles, and melts at 88° .

Thionyl- α -naphthylamine boils at 226° (100 mm.) and melts at 33° ; the condensation derivative with α -naphthylamine and benzaldehyde, $2\text{C}_{10}\text{H}_7\text{NH}_2\cdot\text{SO}_2\cdot\text{PhCHO}$, melts at 84° , and the condensation derivative with aniline and benzaldehyde, $\text{C}_{10}\text{H}_7\text{NH}_2\cdot\text{PhNH}_2\cdot\text{SO}_2\cdot\text{Ph}\cdot\text{CHO}$, melts at 103° .

Thionyl- β -naphthylamine melts at 53° , and the condensation product with β -naphthylamine and benzaldehyde melts at 112° ; that with β -naphthylamine and anisaldehyde melts at 110° .

Thionylorthobromo- β -naphthylamine crystallises in long, yellow needles, melts at 118° , and with salicylaldehyde yields hydroxybenzylideneorthobromo- β -naphthylamine, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\text{Br}$, melting at $144\text{--}145^\circ$.

The *thionyl derivative* of nitro- α -naphthylamine (m. p. 191°) melts at 89° ; and the *thionyl derivative* of nitro- α -naphthylamine (m. p. $118\text{--}119^\circ$) melts at $134\text{--}135^\circ$.

Thionylmetaphenylenediamine melts at 44° , and is slowly decomposed by cold water. *Thionylparaphenylenediamine* melts at $115\text{--}116^\circ$, and is decomposed by hot water. Orthophenylenediamine and thionyl chloride interact, forming Hinsberg's piazthiole (Abstr., 1890, 161).

Thionylmetatoluylenediamine melts at $72\text{--}73^\circ$, and is readily decomposed by water. Orthotoluylenediamine interacts with thionyl chloride, forming methylpiazthiole (*loc. cit.*).

Thionylbenzidine (Abstr., 1891, 717) melts at 82° . *Thionyltolidine* forms reddish-violet needles, and melts at 90° . *Thionyldiamidostilbene*, $\text{C}_2\text{H}_2(\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{SO})_2$, forms red needles, melts at $201\text{--}202^\circ$, and is fairly stable towards water.

A. R. L.

Indene and Hydrindene. By A. SPILKER (*Ber.*, **26**, 1538—1545).—It has already been shown by Krämer and Spilker (Abstr., 1891, 205) that hydrindene, when treated with sulphuric acid, behaves like a methylated benzene derivative, and yields sulphonic acids without formation of any resinous products. The further examination of the product has shown that it is a mixture of two monosulphonic acids, which must correspond in constitution with the α - and β -naphthalene-sulphonic acids, as these are the only two possible forms. No definite proof has yet been obtained as to which is the α - and which the β -derivative, but from their general behaviour it appears probable that the acid formed in the larger quantity has the latter constitution.

β -Hydrindenesulphonic acid, $\text{C}_9\text{H}_8\cdot\text{SO}_3\text{H}$, is best obtained by the action of well-cooled sulphuric acid on hydrindene, and careful addition of a small quantity of water. The upper of the two layers which form is separated and mixed with more water, when it solidifies to a magma of crystals of β -hydrindenesulphonic acid, which contain water of crystallisation, and melt at 92° . The sodium salt crystallises in well developed prisms, which are very soluble in water and contain $4\text{H}_2\text{O}$, three of which are quickly given off in dry air. On treatment with phosphorus pentachloride, it yields a *sulphochloride*, $\text{C}_9\text{H}_7\text{SO}_2\text{Cl}$, which forms colourless, glassy crystals, melts at

45°, and is converted by ammonia into the corresponding *sulphonamide*, $C_9H_7SO_2NH_2$; the latter crystallises in narrow, satiny plates melting at 135·5—136° (corr.). *α-Hydrindenesulphonic acid* is always formed, together with the *β*-compound, the amount varying with the temperature at which the sulphonation is carried out; the acid and all its derivatives are more readily soluble than the corresponding *β*-compounds, and are only separated with difficulty from the latter. The separation is most readily effected with the sulphonamides, the *α-sulphonamide* being obtained in the form of white, nodular, crystalline aggregates melting at 91·5—92·5° (corr.).

In the previous paper, it was mentioned that indene, on treatment with bromine, gives a dibromide, and that this compound, on boiling with water, is converted into a substance supposed by Krämer and Spilker to be bromhydroxyhydrindene; this supposition has proved on further investigation to be correct, and the author has also been able to prepare *dichlorhydrindene*, $C_9H_8Cl_2$, and *chlorhydroxyhydrindene*, $C_9H_8Cl\cdot OH$, in a similar manner from indene, the latter compound crystallising in white, silky needles, and melting at 128—129°. Bromhydroxyhydrindene readily reacts with aqueous ammonia, forming *amidohydroxyhydrindene*, $OH\cdot C_9H_8\cdot NH_2$, and the corresponding *imidodihydroxydihydrindene*, $(OH\cdot C_9H_8)_2NH$. Cold water extracts the hydrobromide of the amido-compound, whilst the imido-base remains behind, and on purification crystallises in fascicular aggregates of white needles, or in long, narrow plates melting at 188·5° (corr.). It yields an *acetyl* derivative crystallising in hard, transparent, cube-shaped crystals, and melting at 220°, and an amorphous *nitroso*-compound. The amidohydroxyhydrindene is obtained from the hydrobromide by the action of alkalis, and crystallises from ether in white plates melting at 132—133°, which readily absorb moisture and carbonic anhydride from the air. The *hydrochloride* crystallises in satiny plates. When treated with nitrous acid, the amido-group is replaced by hydroxyl in the usual manner, yielding *hydrindene glycol*, $C_9H_8(OH)_2$, which may be crystallised from benzene, and then melts at 120°.

When indene is passed through an iron tube heated to bright redness, about 75 per cent. remains unaltered, and the remainder is converted almost entirely into hydrogen and chrysene. H. G. C.

2'. 3'-Diphenylindoles. By A. BISCHLER and P. FIREMAN (*Ber.*, 26, 1336—1349; compare *Abstr.*, 1892, 1465).—Desyl bromide, $COPh\cdot CHPhBr$, like phenacyl bromide, is readily converted into indole derivatives by boiling with aromatic amido-compounds, the corresponding anilides being formed as intermediate products. *Desylanilide*, $COPh\cdot CHPh\cdot NHPh$, is readily obtained by boiling desyl bromide with aniline and a little alcohol, and crystallises in fascicular aggregates of yellow needles. Its *hydrochloride* forms a snow-white, crystalline mass which is decomposed by water, and the *acetyl* derivative crystallises in concentric groups of needles. *Desylparatoluidide*, $COPh\cdot CHPh\cdot NH\cdot C_6H_4Me$, obtained in a similar manner from desyl bromide and paratoluidine, crystallises from alcohol in deep yellow, fascicular aggregates of needles, and its *hydrochloride* forms a nacreous,

crystalline mass which is also decomposed by water; the *acetyl* derivative crystallises from alcohol in characteristic plates, and melts at 150°. *Desyl-β-naphthalide*, $\text{C}_6\text{H}_4\text{CPh}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, also crystallises in fascicular aggregates of needles, and melts at 131—132°; the *hydrochloride* crystallises in white needles.

2'.3'-Diphenylindole, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CPh} \\ \text{NH}\end{smallmatrix}\rangle\text{CPh}$, is obtained by boiling either desylanilide or desylparatoluidide with aniline; the product is fractionated in a vacuum, extracted with light petroleum, and recrystallised from alcohol; it then has the properties assigned to it by Fischer; its *picrate*, $\text{C}_{10}\text{H}_{16}\text{N}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, forms pale-red needles, and melts at 154° with decomposition. *2'.3'-Diphenylparatolindole*, $\text{C}_6\text{H}_3\text{Me}\langle\begin{smallmatrix}\text{CPh} \\ \text{NH}\end{smallmatrix}\rangle\text{CPh}$, is prepared by boiling desylanilide or paratoluidide with paratoluidine, and crystallises in well-developed, fascicular aggregates of needles melting at 153°; its *picrate* forms chocolate-brown needles.

2'.3'-Diphenylorthotolindole, $\text{C}_6\text{H}_3\text{Me}\langle\begin{smallmatrix}\text{CPh} \\ \text{NH}\end{smallmatrix}\rangle\text{CPh}$, obtained by substituting orthotoluidine for paratoluidine, crystallises in four-cornered plates or nodular aggregates of needles, melts at 128°, and forms a *picrate* which crystallises in coffee-brown needles melting at 173°. The solutions of all the above indoles show a blue fluorescence.

1'-Methyl-2'.3'-diphenylindole, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CPh} \\ \text{NMe}\end{smallmatrix}\rangle\text{CPh}$, is prepared by boiling desylanilide with methylaniline, and crystallises in concentric groups of nacreous needles melting at 139°; the *picrate* forms brownish-red needles, and melts at 158°. *2'.3'-Diphenyl-β-naphthylindole*, $\text{C}_{10}\text{H}_6\langle\begin{smallmatrix}\text{CPh} \\ \text{NH}\end{smallmatrix}\rangle\text{CPh}$, is formed by boiling desyl-β-naphthalide with β-naphthylamine, and distilling the product under diminished pressure; it is separated with difficulty from the dinaphthylamine simultaneously formed, and crystallises in nodular aggregates of needles melting at 153—158°; it readily yields a *picrate* which forms flesh-coloured needles, and decomposes without melting at 155°.

Desylanilide is acted on by orthodiamines in quite a different manner to the monamines, derivatives of quinoxaline being formed; thus desylanilide and orthotoluylenediamine yield the diphenyltolu-quinoxaline, $\text{C}_6\text{H}_3\text{Me}\langle\begin{smallmatrix}\text{N:CPh} \\ \text{N:CPh}\end{smallmatrix}\rangle$, already described by Hinsberg (*Annalen*, 237, 327).

H. G. C.

Dihydromethylketole. By E. BAMBERGER and H. STERNITZKI (*Ber.*, 26, 1291—1307).—Dihydromethylketole is converted by nitrous acid into the nitrosamine, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}_2- \\ \text{N(NO)}\end{smallmatrix}\rangle\text{CHMe}$, which has been obtained in beautiful prisms belonging to the rhombic system, $a:b:c = 0.4673:1:1.5398$. When this compound, dissolved in dry ether, is treated with absolute alcoholic hydrogen chloride, it is converted into the isomeric *paramitrosodihydromethyl-*

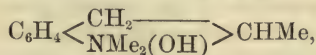
ketole, $\text{NO} \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \end{smallmatrix} > \text{CHMe}$. This crystallises in small, yellow needles, melts at $103\text{--}105^\circ$, and yields pure green solutions. The *hydrochloride* forms small, yellowish-brown crystals, darkens at 160° , melts at 168° with decomposition, and when reduced with tin and hydrochloric acid, yields paramidodihydromethylketole (see this vol., i, 469).

Dinitrosodihydromethylketole, $\text{NO} \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{CH}_2 \\ \text{N(NO)} \end{smallmatrix} > \text{CHMe}$, is obtained by adding sodium nitrite to an aqueous solution of the above hydrochloride. It crystallises in slender, moss-green needles, and melts at $105\text{--}106^\circ$.

Nitronitrosodihydromethylketole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{CH}_2 \\ \text{N(NO)} \end{smallmatrix} > \text{CHMe}$, is obtained by shaking the nitrosamine of the hydroketole with dilute nitric acid. It crystallises in lustrous leaflets, melts at $133\cdot5^\circ$, and does not give the nitroso-reaction.

n-Methyldihydromethylketole, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_2 \\ \text{NMe} \end{smallmatrix} > \text{CHMe}$, is obtained by gradually adding methylic iodide to well-cooled hydromethylketole, and completing the reaction by heating on the water-bath. It is a colourless oil, boils at $222\text{--}225^\circ$ under 722 mm. pressure, and is very similar to *n*-methyltetrahydroquinoline. The *methiodide* crystallises in beautiful, colourless prisms, and melts at 211° .

n-Dimethyldihydromethylketolium hydroxide,

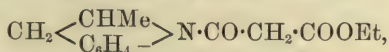


is obtained by shaking the preceding methiodide with silver hydroxide. It crystallises in long, lustrous needles, and decomposes at 100° to yield methyl alcohol and methyldihydromethylketole.

Nitro-n-methyldihydromethylketole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{CH}_2 \\ \text{NMe} \end{smallmatrix} > \text{CHMe}$, is obtained by treating the tertiary base dissolved in sulphuric acid with potassium nitrate. It crystallises in dark red needles, melts at $48\text{--}49^\circ$, and is soluble in dilute mineral acids.

Dihydromethylketole condenses with ethylic acetoacetate and ethylic malonate in a similar way to tetrahydroquinoline, and yields compounds of the same type as juloline. The author proposes to name the simplest compound *liloline*. In the case of dihydromethylketole, a better yield of the condensation product is obtained with ethylic malonate than with ethylic acetoacetate, and also the intermediate bicyclic anilide has been isolated.

Ethylic dihydromethylketolyl- β -ketopropionate,



is obtained by cautiously heating molecular proportions of dihydromethylketole and ethylic malonate on the sand-bath for seven hours. If the temperature is allowed to rise to $240\text{--}250^\circ$, a further action takes place, and the *lilolidine* is formed. It crystallises in long,

prismatic needles, melts at 209° , and in alcoholic solution gives a deep reddish-brown coloration with ferric chloride. It is easily soluble in alkalis, and is precipitated unchanged by acids. The aqueous solution of the sodium salt gives insoluble precipitates with many metallic salts. The *barium* salt forms small, transparent crystals.

α_1 -Methyl- α_1 -diketolilolidine, $C_6H_5\langle\frac{CH_2-CH_2}{CO\cdot CH_2\cdot CO}\rangle N$, is obtained by heating the preceding compound with concentrated hydrochloric acid at 150 — 160° . It crystallises in white, nacreous leaflets, melts at 298° , and is soluble in concentrated mineral acids and in alkalis. The sodium salt gives insoluble precipitates with salts of the heavy metals. The *hydrochloride* crystallises in long, colourless needles, and decomposes, on exposure to air, into hydrogen chloride and the free base. When treated with sodium nitrite in acetic acid solution, it yields a bluish-green dye, and a *nitroso-derivative* which crystallises in small, spherical aggregates, and melts at 151 — 152° .

Benzoyldihydromethylketole, when oxidised in alkaline solution with potassium permanganate, yields the following products:—Benzoylanthranilic acid, 56 per cent.; benzoic acid, 32 per cent.; acetylanthranilic acid, 1 per cent.; benzamide, 0.5 per cent.; a trace of methylketole, and a large quantity of oxalic acid.

Benzoyldihydromethylketole, $C_6H_5\langle\frac{CH_2}{NBz}\rangle CHMe$, crystallises in beautiful, transparent prisms, and melts at 91.5° .

To determine the position of the nitroso-group in nitrosodihydromethylketole, the author has endeavoured to prepare paramidodihydromethylketole synthetically by converting paranitrophenylhydrazine into paranitrophenylhydrazoneacetone, and treating the latter with stannous chloride and then with reducing agents.

Paranitrophenylhydrazoneacetone crystallises in long, golden-yellow needles, and melts at 148 — 148.5° . When heated with stannous chloride, it yields a brown melt, and on subjecting this to steam distillation, a compound is obtained which crystallises in colourless needles, and melts at 61 — 62° . A nitromethylketole could not be isolated from the product.

E. C. R.

Action of Phenylhydrazine on Lactones. By J. EPHRAIM (*Ber.*, 26, 1376—1378; compare Meyer and Saul, this vol., i, 473).—When the unsaturated lactone benzalphanthalide is heated with phenylhydrazine, condensation occurs, and a substance is obtained which crystallises in white needles melting at 171 — 172° , and is not affected by hydrochloric acid at 180° . It may also be obtained by heating deoxybenzoïnorthocarboxylic acid with phenylhydrazine in alcoholic solution, and is doubtless a derivative of phthalazone (this vol., i, 346), 3-phenyl-1-benzylphthalazone, $CO\langle\frac{C_6H_5}{N_2Ph}\rangle C\cdot CH_2Ph$.

C. F. B.

Phenylnaphthalenes and Zincke's Hydrocarbon $C_{16}H_{12}$. By R. MÖHLAU and R. BERGER (*Ber.*, 26, 1196—1200).—By the inter-

action of solid diazobenzene chloride and naphthalene in presence of aluminium chloride, α - and β -phenylnaphthalenes are formed, together with benzeneazonaphthalene and chlorobenzene; the product is treated with stannous chloride and hydrochloric acid, and, on purification and subsequent distillation, the phenylnaphthalenes are obtained in the fraction boiling above 260° under a pressure of 160 mm. The yield from 110 grams of aniline hydrochloride is 54.5 grams, nine-tenths of which consists of the α -derivative.

α -Phenylnaphthalene is separated from the β -compound by freezing; it is a pale yellow liquid with a faint blue fluorescence, boiling at 324 — 325° ; on oxidation with potassium permanganate in acid solution, orthobenzoylbenzoic acid is formed.

β -Phenylnaphthalene crystallises from dilute alcohol in slender, lustrous plates, melts at 101 — 102° , and is volatile with steam; on oxidation with chromic anhydride in acetic acid solution, it is converted into a quinone, $C_{16}H_{10}O_2$ (m. p. 109 — 110°), which is identical with that obtained by Zincke and Breuer from the hydrocarbon formed by the interaction of phenyl glycol and phenylacetaldehyde.

J. B. T.

Essential Oil of Niaouli. By G. BERTRAND (*Compt. rend.*, 116, 1070—1073).—Essential oil of niaouli, obtained from *Melaleuca viridiflora*, a tree which grows abundantly in New Caledonia, is a pale yellow oil with a greenish tinge, and a sweet odour resembling that of oil of cajeput. It is prepared by distilling the leaves with water, the yield being 2.5 per cent. of the weight of the leaves. It is somewhat viscous and is dextrogyrate; sp. gr. at $12^{\circ} = 0.922$.

Essential oil of niaouli contains minute quantities of valeric acid, ethylic valerate, benzaldehyde, and amyl alcohol. It consists chiefly of a terebenthene boiling at 155 — 156° and a liquid boiling at 173 — 175° . The terebenthene is a mobile liquid with the usual odour of terebenthene; sp. gr. at $12^{\circ} = 0.865$; specific rotatory power $[\alpha]_D = +36^{\circ} 3'$. It yields a crystalline hydrochloride which in alcoholic solution has a specific rotatory power $[\alpha]_D +25^{\circ} 9'$.

The fraction boiling at 173 — 175° when cooled to -6° yields crystals of an eucalyptol, which melts at 1° and boils at 175° ; sp. gr. at $12^{\circ} = 0.930$; vapour density = 5.28. When treated with dry hydrogen chloride at -10° , it yields a crystalline, unstable compound, $2C_{10}H_{18}O.HCl$, which is immediately decomposed by water with separation of eucalyptol. The portion remaining liquid at -6° is a mixture of the eucalyptol with a citrene having a levorotatory power of about -20° .

The smaller fraction of the original oil boiling above 180° consists of a terpinol having a levorotatory power of $[\alpha]_D = -2^{\circ} 10'$.

It is noteworthy that, leaving aside the terebenthene, oil of niaouli contains eucalyptol, a citrene, and a terpinol, and in this respect resembles the terpinol obtained by List by the action of dilute acids on the terpin resulting from the spontaneous hydration of terpenes.

C. H. B.

Liquid Isomeride of Hydrocamphene. By L. BOUVEAULT (*Compt. rend.*, 116, 1067—1070).—The product obtained by the action of dry hydrogen chloride on oil of turpentine was heated to

boiling and gradually mixed with sufficient sodium to remove the whole of the chlorine, and the product was repeatedly fractionated, the hydrocamphene being removed by repeated cooling and crystallisation. A fraction was thus obtained boiling at 148–151° and yielding no crystals when cooled; its composition corresponded with a mixture of 75 parts of a hydrocarbon $C_{10}H_{18}$ and 25 parts of a hydrocarbon $C_{10}H_{16}$. Treatment of this fraction with hydrogen chloride does not remove the whole of the terpene, but this is readily effected by treatment with bromine in chloroform solution, and on fractionating the product, a colourless liquid boiling at 148–149° is obtained. It has the composition $C_{10}H_{18}$, and its vapour density corresponds with the molecular weight 138. This liquid, which has a faint odour of oranges, is isomeric with hydrocamphene, from which it is readily distinguished by its boiling point and the fact that it does not crystallise. It seems also to be isomeric with the camphene hydride obtained by Berthelot by the action of hydrogen iodide on oil of turpentine.

The new hydrocarbon is not attacked by bromine or by fuming sulphuric acid at the ordinary temperature. The author calls it provisionally *hydropinene*.
C. H. B.

Action of Zinc on Chlorocamphor: Relation between Camphor and Carvacrol. By A. ÉTARD (*Compt. rend.*, 116, 1136–1139).—When monochlorocamphor mixed with about 10 per cent. of zinc chloride is boiled without distillation until evolution of hydrogen chloride ceases and is then distilled, carvacrol is obtained in quantity corresponding with 65 per cent. of the calculated yield. At the same time some carbonic oxide is evolved and a hydrocarbon C_9H_{16} is formed. It boils at 137°; sp. gr. at 15° = 0.795; index of refraction $[n]_D = 1.434$, $R = \frac{n^2 - 1}{n^2 - 2d} M = 40.58$. The value calculated on the assumption that there are no double bonds is 39.32. This hydrocarbon seems to be identical with the campholene of de Lalande, Kachler, and Zürer. It would follow, therefore, that the benzene ring has been broken and the campholene corresponds with the camphorone that yields α -methylglutaric acid on oxidation. The hydrocarbon C_9H_{14} , from which campholene is supposed to be derived, cannot be a tetrahydro-xylene, for it is derived from camphoric anhydride or copper camphorate with loss of carbonic anhydride.

Chlorocamphor seems to behave as a hydrochloride of carvacrol and in this respect is strictly analogous to carvol hydrochloride. It follows that camphor may be regarded as a hydrocarvacrol, and the fact that it does not dissolve in alkalis is not surprising in view of the fact that the phenolic function of carvacrol itself is very weak and is necessarily diminished by hydrogenation.
C. H. B.

Camphoric acid Derivatives. By H. RUPE and C. MAULL (*Ber.*, 26, 1200–1202).—Bromocamphoric anhydride is readily prepared according to Volhard's method by the action of bromine and phosphorus on camphoric anhydride; it easily reacts with certain bases,

crystalline compounds of the type $\text{NHR} \cdot \text{C}_8\text{H}_{13}\text{C}_2\text{O}_3$ have been obtained with aniline, paratoluidine, phenylhydrazine, and piperidine. The *anilidoanhydride* melts at 123° and on hydrolysis with soda, yields the corresponding *acid*, which melts at 154° .

By the action of hydrochloric acid on the anilidoanhydride, hydroxycamphoric acid lactone (camphanic acid), $\text{COOH} \cdot \text{C}_8\text{H}_{13} \begin{smallmatrix} \text{O} \\ | \\ \text{CO} \end{smallmatrix}$, is formed.

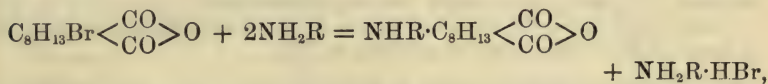
On treatment of bromocamphoric lactone with zinc-dust and acetic acid, camphoric acid is regenerated.

The formation of tetrahydro-xylene from water and camphanic acid, as observed by Wreden, cannot be confirmed; a mixture of lauronic acid and camphoric lactone, which boils at 210° , appears to be the only product.

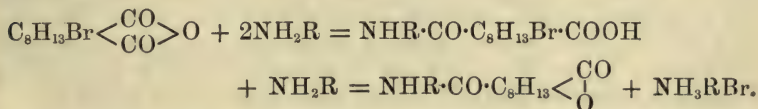
Tetrahydro-xylene is obtained by the distillation of calcium camphanate; it boils at $118\text{--}122^\circ$, and instantaneously decolorises potassium permanganate and bromine water.

J. B. T.

Camphoric acid. By K. AUWERS and H. SCHNELL (*Ber.*, 26, 1517—1532).—The action of bases on bromocamphoric anhydride does not take place, according to the authors, in correspondence with the equation



as Rupe and Maull (preceding abstract) assert, but rather with the equations



Thus what Rupe and Maull supposed to be anilidocamphoric anhydride is the anilide of camphanic acid. The chief evidence in favour of this view is that the acid obtained from such a compound by the action of soda is monobasic, not bibasic.

Camphoramie acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_8\text{H}_{14} \cdot \text{COOH}$, prepared from camphoric anhydride and aqueous ammonia, melts at $174\text{--}175^\circ$, and, when pure, easily gives off ammonia on boiling with dilute soda (compare Claisen and Manasse, this vol., i, 479).

Camphormethylamic acid, $\text{NHMe} \cdot \text{CO} \cdot \text{C}_8\text{H}_{14} \cdot \text{COOH}$, obtained from camphoric anhydride and 33 per cent. methylamine solution, when recrystallised from aqueous acetone, forms rhombic prisms, and melts at 225° . It is a monobasic acid easily soluble in hot water.

Camphordimethylamic acid, $\text{NMe}_2 \cdot \text{CO} \cdot \text{C}_8\text{H}_{14} \cdot \text{COOH}$, forms long, pointed prisms, and melts at $186\text{--}187^\circ$. It dissolves with decomposition in hot water.

Bromocamphoric anhydride, when heated with water, yields camphanic acid, and, when warmed for two hours on the water-bath

with aqueous alcohol containing a little potassium cyanide, gives *ethylic camphanate*. This salt melts at 62° and boils at 195—196°.

Camphanamide is formed when dry ammonia is led into a solution of bromocamphoric anhydride in boiling chloroform. It may also be produced by acting, at the ordinary temperature, on ethylic camphanate with aqueous ammonia. It melts at 208°, is easily soluble in water, alcohol, hot benzene, and chloroform, and insoluble in light petroleum. By heating with 10 per cent. potash solution, it may be converted into *hydroxycamphoramic acid*, $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_8\text{H}_{13}(\text{OH}) \cdot \text{COOH}$, melting at 155—156°. The calcium salt crystallises with 2 mols. of water.

Camphanmethylanide is the product of the interaction of bromocamphoric anhydride and methylamine solution, much heat being evolved on its formation. It melts at 133°, and is soluble in water, and organic solvents except light petroleum. It is easily converted by dilute potash solution into the potassium salt of *hydroxycamphor-methylanilic acid*, $\text{NHMe} \cdot \text{CO} \cdot \text{C}_8\text{H}_{13}(\text{OH}) \cdot \text{COOH}$, which melts at 156° with decomposition.

Camphananilide is formed in boiling chloroform solution from aniline and bromocamphoric anhydride. It melts at 126°, is insoluble in water, but soluble in alcohol, ether, chloroform, and benzene. It is transformed into *hydroxycamphoranilic acid* by heating in alcoholic solution with slight excess of potash, and acidifying. This acid melts at 151° and passes easily into camphananilide.

Camphanphenylhydrazide is obtained in the same way as the anilide. It forms white, silky needles melting at 193°. J. W.

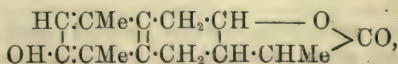
Bromal Borneolates. By J. MINGUIN (*Compt. rend.*, 116, 889—891).—Bromal combines readily with the various modifications of borneol, forming products which can be crystallised from toluene. The borneolates formed have the composition $\text{CBr}_3 \cdot \text{CH}(\text{OH}) \cdot \text{OC}_{10}\text{H}_{17}$. That derived from racemic borneol crystallises well only from light petroleum. The products from the borneols have the following melting points and molecular rotatory powers when dissolved in toluene.

	M. p.	Rotatory power.
Dextrogyrate borneol	105—109°	$[\alpha]_D = +52.4^\circ$
Lævogryrate „	105—109	$[\alpha]_D = -52.4$
Racemic „	79— 82	$[\alpha]_D = 0$

The inactive borneol ($\alpha\beta$ -) yields a viscous, non-crystallisable liquid, with a rotatory power $[\alpha]_D = -3.4^\circ$.

Combination of bromal with the isocamphols takes place somewhat less readily, but the products are similar. C. H. B.

New Isomerides of Santonin and Santonous acid. By A. ANDREOCCHI (*Ber.*, 26, 1373—1376).—When santonin is dissolved in fuming hydrochloric acid, and the solution allowed to remain in a cool place, *desmotroposantonin* crystallises out. This substance is isomeric with santonin, and has the constitution



the $\text{CH}_2\cdot\text{CO}$ group of santonin having been doubtless converted into $\text{CH}\cdot\text{C}(\text{OH})$. It forms small, white needles, melts at 260° when quickly heated, and has specific rotation $+112^\circ$. It has lost the ketonic properties of santonin, but has acquired phenolic properties, for it yields an *acetyl derivative*, melting at 156° . It retains the lactonic properties of santonin. When reduced with zinc and acetic acid, it yields *desmotroposantonous acid* (*dimethylhydroxytetrahydronaphthylpropionic acid*), $\text{C}_{15}\text{H}_{20}\text{O}_3$, which melts at 175° , has the specific rotation -53.3° , is converted, by fusion with potash into propionic acid and dimethylnaphthol ($\text{Me}_2 : \text{OH} = 1 : 4 : 3$), and is isomeric with santonous acid. C. F. B.

Dihydroxypyridines. By S. RUHEMANN (*Ber.*, **26**, 1559—1561; compare *Trans.*, 1893, 259, 874).—The author points out the strong analogy which exists between the α' -dihydroxypyridines and resorcinol; the former yield, with phthalic anhydride, phthaleïns having a red odour and blue fluorescence, and give, with ferric chloride in aqueous solution, yellow colouring matters, which are probably hydroxyquinones. Resorcinol and its derivatives yield colouring matters when oxidised in ammoniacal solution, and the dihydroxypyridines behave in a similar manner; the colouring matters formed have a cantharidin lustre, and dissolve in alcohol with a bluish colour, and in acetic acid with reddish-violet colour. They are at present undergoing further investigation.

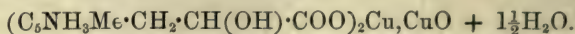
Bromine acts on dihydroxypyridines, with formation of substitution products; thus, methyl-dihydroxypyridine yields a *dibromo-derivative*, $\text{C}_6\text{H}_5\text{Br}_2\text{NO}_2$, which crystallises in yellow needles, and melts with decomposition at 145° . It is not affected by warm water or cold dilute potash, but decomposes on boiling with either water or alkalis.

H. G. C.

Action of Chloral on Pyridine Bases from Messel. By A. EINHORN and A. W. GILBODY (*Ber.*, **26**, 1414—1422).—A mixture of pyridine bases, obtained in distilling the bituminous shale of Messel, near Darmstadt, was separated into two portions, boiling respectively below 137° and from 137° to 160° , and these portions were treated separately with chloral, as described in *Abstr.*, 1892, 75. From the first, the compound of chloral with 2-picoline was isolated; from the second, a compound with 2:6-lutidine, hitherto unknown.

2:6-Picolyl- ω -trichloro- α -hydroxypropane (2:6-lutidine chloral), $\text{C}_6\text{NH}_3\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$, forms small, lustrous tables melting at 105.5° . The *hydrochloride* (+ H_2O) crystallises in cubes, melting at 134° ; the *hydrobromide* in small plates, melting at 113.5° ; the *platinochloride* in orange-coloured plates, melting with decomposition at 210° ; and the *aurochloride* in yellow, transparent needles, melting at 165° . When the hydrochloride is boiled with alcoholic potash in excess, 2:6-picolylacrylic acid, $\text{C}_6\text{NH}_3\text{Me}\cdot\text{CH}\cdot\text{CH}\cdot\text{COOH}$, is obtained; it forms rhombic tables, melting at 169.5° ; the *hydrochloride* crystallises in small plates, melting at 234° ; and the *platinochloride* in lustrous, yellow crystals, melting with decomposition at 231° ; metallic salts may also be prepared. If, instead of alcoholic potash, aqueous sodium carbonate is used, then 2:6-picolyl- α -hydroxypropionic (2:6-picolyl-

lactic) acid, $C_5NH_3Me \cdot CH_2 \cdot CH(OH) \cdot COOH$, is obtained, and may be isolated by means of the copper salt; it forms tiny, quadrangular crystals, melting at 166° . The *platinochloride* forms orange-red crystals, melting at 185° ; the *aurochloride* (+ H_2O) yellow tables, melting at 100° , when anhydrous at 143 – 144° . The normal *copper salt* is blue, and, when recrystallised from boiling water, is partially decomposed into the green basic salt,



C. F. B.

Tetrahydroisoquinoline. By E. BAMBERGER and W. DIECKMANN (*Ber.*, 26, 1205–1221).—In spite of the close similarity of quinoline and isoquinoline in properties, the tetrahydro-derivatives of these compounds should exhibit considerable differences, since tetrahydroquinoline, $C_6H_4 < \begin{smallmatrix} CH_2 \cdot CH_2 \\ | \\ NH \cdot CH_2 \end{smallmatrix}$, may be regarded as an alkylaniline, but

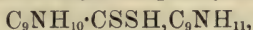
tetrahydroisoquinoline, $C_6H_4 < \begin{smallmatrix} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot NH \end{smallmatrix}$, as a benzylamine base,

closely related to piperidine; this proves to be correct, as the latter has an alkaline reaction, readily combines with carbonic anhydride and carbon bisulphide, and with diazo-compounds yields diazoamido-derivatives. The preparation of tetrahydroisoquinoline from commercial isoquinoline containing 60 per cent. of quinoline is described. The following reactions, in addition to those already known, serve to characterise the base; potassium dichromate does not give either a precipitate or a coloration; bromine water gives a yellow, oily precipitate; potassium ferrocyanide produces a colourless salt, crystallising in needles; with benzoquinone, a red coloration is obtained, changing to carmine on warming; calcium hypochlorite gives an oily chlorimide, the alcoholic solution of which produces, with aniline and hydrochloric acid, a green colour, changing to violet-red on warming. The *mercuriochloride* is crystalline, and melts at 151° ; the *picrate* crystallises in lustrous, yellow needles melting at 195° .

The authors remark that the hydroquinolines also give characteristic colours with quinone, tetrahydroquinoline yielding a deep violet-blue coloration.

Diazoamidobenzenetetrahydroisoquinoline, $C_9NH_{10} \cdot N_2Ph$, is prepared by the action of diazobenzene nitrate or chloride on tetrahydroisoquinoline in presence of sodium acetate, and crystallises from light petroleum in colourless, long, prismatic plates, melting at 61.5° . The compound exhibits all the properties of the diazoamido-derivatives, gives a red coloration with molten resorcinol, a violet-red colour with glacial acetic acid and α -naphthylamine, whilst, on heating with acids, the original base is regenerated, together with phenol and nitrogen; it does not explode when heated. The *picrate* crystallises in needles.

Nitrosotetrahydroisoquinoline, $C_9NH_{10} \cdot NO$, is formed by heating the tetrahydro-base with sodium nitrite and dilute hydrochloric acid, and crystallises from light petroleum in slightly coloured, strongly refractive, fat needles, melting at 53° ; it is soluble in concentrated hydrochloric acid, from which it is precipitated unchanged on dilution.

Tetrahydroisoquinoline tetrahydroisoquinoyldithiocarbamate,

crystallises from alcohol in colourless needles, which, after previous softening, melt at $173\text{--}174^\circ$ with decomposition. The *copper salt* is reddish-brown and amorphous; the *lead salt* is colourless and amorphous; the *mercuric salt* is crystalline; the *silver salt* pale yellow, turning black on warming.

Tetrahydroisoquinoylcarbamide, $\text{C}_9\text{NH}_{10}\cdot\text{CONH}_2$, crystallises in colourless, lustrous plates, melting at 169° .

Phenyltetrahydroisoquinoylcarbamide, $\text{C}_9\text{NH}_{10}\cdot\text{CO}\cdot\text{NHPh}$, is deposited from alcohol in stellate groups of slender needles, melting at 144° .

Phenyltetrahydroisoquinoylthiocarbamide, $\text{C}_9\text{NH}_{10}\cdot\text{CS}\cdot\text{NHPh}$, crystallises from alcohol in slender, lustrous needles, and melts at 140° . Attempts to methylate the tetrahydro-base were unsuccessful; by the action of methylic iodide, the quaternary iodide is formed, and is deposited from alcohol in lustrous needles or plates melting at 189° .

Acetyltetrahydroisoquinoline is crystalline, melts at 46° , and boils at $220\text{--}225^\circ$ under a pressure of 70 mm. The *benzoyl derivative* forms highly refractive, rhombic crystals, melts at 129° , and boils with decomposition at $245\text{--}250^\circ$ under a pressure of about 50 mm.

Benzoyltetrahydroisoquinoline, on oxidation with potassium permanganate in alkaline solution, yields *ortho- ω -benzoylamidoethylbenzoic acid*, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHBz}$, which closely resembles benzoylamidovaleric acid and benzoylhomoconiic acid from piperidine and coniine respectively; the acid is insoluble in benzene and light petroleum, and crystallises from water or ethylic acetate in clusters of silky, lustrous needles or prisms, which melt at 172° ; it is soluble in concentrated hydrochloric acid, is reprecipitated on dilution, and appears to be without physiological action. The yield is 50—60 per cent., benzoic acid (15 per cent.), benzamide (6 per cent.), phthalic acid (20 per cent.), and traces of oxalic acid being also formed, together with a ketonic acid, which could not be isolated. The salts of the heavy metals are almost all extremely sparingly soluble; the *silver salt* is crystalline and stable towards light; the *lead salt* is amorphous and soluble in chloroform or alcohol; the *copper, barium, and calcium salts* crystallise in small, lustrous plates.

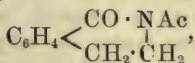
Benzoylhydroisocarbostyryl, $\text{C}_6\text{H}_4\cdot\begin{smallmatrix} \text{CO}\cdot\text{NBz} \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}$, is prepared by heating the acid with acetic anhydride, and crystallises from alcohol in long, lustrous prisms and in slender needles melting at 132° ; the compound is hydrolysed by soda, with formation of benzoic acid and hydroisocarbostyryl (see below).

Amidoethylbenzoic acid, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, is obtained, together with benzoic acid and hydroisocarbostyryl (see below), by heating benzoylamidoethylbenzoic acid with concentrated hydrochloric acid in a sealed tube at $150\text{--}160^\circ$; after purification and treatment of the hydrochloride with silver oxide in alcoholic solution, the acid crystallises in small, lustrous, highly refractive needles, which melt at $160\text{--}165^\circ$. The *salts* formed both with mineral acids and

heavy metals are readily soluble in water. The yield is 30 per cent. of the benzoylamido-acid employed, together with an equal quantity of hydroisocarbostyryl. The *hydrochloride* crystallises from alcohol in colourless plates melting at 199—200°. The *platinochloride* is deposited from water in slender, yellow needles, which melt at 230° with decomposition.

Hydroisocarbostyryl, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CO} \cdot \text{NH} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$ (*dihydroisoquinolone*), is

formed by heating benzoylhydroisocarbostyryl with soda; by heating the benzoyl-acid with hydrochloric acid (see above); by the evaporation of the amido-acid or the hydrochloride in aqueous solution, or by heating the amido-acid above its melting point; it is most readily prepared by distillation of the benzoyl-acid, benzoic acid and a little benzonitrile being also formed; it crystallises from light petroleum in groups of lustrous needles, melts at 70—71°, and boils above 300° without decomposition. The compound closely resembles the alkaloids; it produces dilation of the pupil, gives white, flocculent precipitates with phosphomolybdic acid and with phosphotungstic acid, which crystallise from water; with solutions of iodine in potassium iodide and of potassium bismuthiodide, reddish-brown precipitates are produced; it is unaffected by heating with moderately concentrated hydrochloric acid, and is scarcely acted on by 10 per cent. potash. Attempts to prepare a methyl derivative were unsuccessful, and it could not be converted into isocarbostyryl, nor could the latter compound be reduced to the quinolone. The *acetyl derivative*,



is deposited from dilute alcohol in lustrous crystals, which melt at 100°. J. B. T.

Phenometadiazine Derivatives. By A. BISCHLER and E. BURKART (*Ber.*, 26, 1349—1353; compare *Abstr.*, 1891, 745; this vol., i. 47).—In addition to the phenometadiazines already prepared by Bischler's method, the authors have prepared two oxyphenometadiazines by the action of ammonia on acetyl-orthamidobenzoic acids. Thus, when the ammonium salt of formylorthamidobenzoic acid is heated, it loses water and is converted into 4'-oxyphenometadiazine

$\text{C}_6\text{H}_4 < \begin{array}{c} \text{N} = \text{CH} \\ | \\ \text{CO} \cdot \text{NH} \end{array}$, which has been prepared in a different manner by

Weddige. The acetyl derivative of orthamidobenzoic acid gives the methyl derivative of this compound, which has also been described by Weddige. When acetylorthamidoacetophenone is heated with

ammonia, it yields 2' : 4'-dimethylphenometadiazine, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{N} = \text{CMe} \\ | \\ \text{CMe} \cdot \text{N} \end{array}$;

the latter is a thick, yellow oil, with a deep yellowish-green fluorescence, which boils at 249° under a pressure of 713 mm., and readily combines with 2H₂O, to form a crystalline hydrate; the latter forms snow-white, satiny, felted needles, melts at 72°, and loses water over sulphuric acid or on warming. Its *picrate*, C₁₀H₁₀N₂·C₆H₃N₃O₇, forms

yellowish, crystalline crusts, and melts at 170° with complete decomposition.

In order to obtain the corresponding methylphenometadiazine, the author endeavoured to prepare the corresponding formylorthamidoacetophenone by heating the amidoketone with formic acid. The resulting product has, however, the formula $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{N} = \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \end{smallmatrix}$ and is formed by the condensation of 2 mols. of the amidoketone with elimination of water; the amido-group is then acted on by the excess of formic acid with formation of the formyl derivative. The first compound is isomeric with flavaniline, and may therefore be termed *isoflavaniline*. The formyl derivative crystallises from alcohol in short, chamois yellow needles, and melts at 107° ; it is dissolved by concentrated hydrochloric acid, and, on warming, isoflavaniline hydrochloride separates as a pink powder which decomposes on heating without melting. Its solutions have a deep yellow colour.

H. G. C.

Phenometadiazine Derivatives. By A. BISCHLER and F. J. HOWELL (*Ber.*, **26**, 1384—1399; compare *Abstr.*, 1891, 745, this vol., i, 47, and preceding abstract).—2':4'-Dimethylphenometadiazine (preceding abstract) is a colourless oil which boils at 249° , and has sp. gr. 1.0980 at 16° . The *hydrochloride* (+ 1HCl) is a white powder. When reduced with sodium in hot amyl alcoholic solution, it yields *tetrahydroadimethylphenometadiazine*, $\text{C}_{10}\text{H}_{14}\text{N}_2$, which was obtained in an impure state as a dark-coloured oil which boiled at $235\text{--}242^{\circ}$, had sp. gr. 1.0981 at 16° , gave Liebermann's nitroso-reaction, and yielded a *dibenzoyl* derivative, as large, colourless prisms melting at 155° , and a *diacetyl* derivative as small, silky needles melting at 110° .

Propionamidoacetophenone forms large plates melting at 68° .

4'-Methyl-2'-ethylphenometadiazine, $\text{C}_8\text{H}_7 \begin{smallmatrix} \text{N} = \text{CEt} \\ \diagup \quad \diagdown \\ \text{CMe} \cdot \text{N} \end{smallmatrix}$, is a colourless oil which boils at $259\text{--}260^{\circ}$, has sp. gr. 1.0723 at 16° , and solidifies when allowed to remain over sulphuric acid; the *hydrochloride* forms a white, deliquescent mass; the *picrate* a yellow, crystalline powder.

Butyramidoacetophenone forms colourless prisms, melting at 52° . 4'-Methyl-2'-propylphenometadiazine forms a colourless oil which boils at $269\text{--}270^{\circ}$, and has sp. gr. = 1.0546 at 16° ; the *picrate* forms a yellow, the *platinochloride* a reddish-yellow, and the *hydrochloride* a deliquescent, white, powder.

Isobutyramidoacetophenone forms large prisms melting at 50° . 4'-Methyl-2'-isopropylphenometadiazine is a colourless oil which boils at $268\text{--}269^{\circ}$, has sp. gr. 1.0556 at 16° , and solidifies partially on standing; the *platinochloride* forms a reddish-yellow, the *picrate* a bright-yellow, powder.

Benzamidoacetophenone forms small needles melting at 98° . 4'-Methyl-2'-phenylphenometadiazine melts at 90° , and forms stellate clusters of white needles; the *picrate* forms a bright-yellow, the *hydrochloride* a white, mass.

Phenylacetamidoacetophenone forms colourless prisms melting at 79° . *4'-Methyl-2'-benzylphenometadiazine* melts at 76° , and forms colourless needles or plates.

Cinnamylamidoacetophenone, $\text{COMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH} : \text{CHPh}$, forms large, rhombic tables melting at 91° . *4'-Methyl-2'-phenylethenylphenometadiazine* forms colourless needles melting at 96° , and yields an unstable dibromide. The *hydrochloride* and *picrate* form yellow, crystalline powders.

Chloracetamidoacetophenone forms white needles melting at 81° . When heated with ammonia, it yields a mixture of different phenometadiazines; probably it first forms monochlorodimethylphenometadiazine, and the chlorine atom in this reacts with excess of ammonia yielding primary, secondary, and tertiary amines.

Trichloracetamidoacetophenone crystallises in needles.

Oxidation of Phenometadiazines.—Phenometadiazines are not readily oxidised by chromic acid or permanganate. With the former, *4'-methyl-2'-phenylphenometadiazine* yields a little *2'-phenylphenometadiazine*; by the latter *dibenzoyltetrahydrodimethylphenometadiazine* is oxidised to oxalic and benzoic acids.

Synthesis of Quinoline Derivatives.—In the mother liquor from *4'-methyl-2'-benzylphenometadiazine* was contained a *phenylmethyl-oxyquinoline*, $\text{C}_6\text{H}_4 < \begin{matrix} \text{NH} - \text{CO} \\ \text{CMe} : \text{CPh} \end{matrix}$, which had been doubtless formed

by direct condensation, without participation of ammonia, of the *phenylacetamidoacetophenone*, from which it can also be obtained by the action of cold alcoholic potash. It forms long, silky needles melting at 275° . In a similar manner there was obtained from *acetamidoacetophenone* a small quantity of a *methyloxyquinoline*, melting at 221° , identical with the *oxylepidine* prepared by Knorr from *acetacetanilide*.
C. F. B.

Oxazolines and Thiazolines. By A. SALOMON (*Ber.*, 26, 1321—1330).—*Bromethylorthotoluamide*, $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Me}$, is obtained by shaking bromethylamine hydrobromide with aqueous sodium hydroxide and orthotoluic chloride. It crystallises in lustrous scales, melts at $70-71^{\circ}$, and is not very stable.

μ-Orthotolylloxazoline, $\begin{matrix} \text{CH}_2\text{O} \\ \text{CH}_2\text{N} \end{matrix} \gg \text{C} \cdot \text{C}_6\text{H}_4\text{Me}$, is obtained by treating the preceding compound with an alkali. It boils at $254-255^{\circ}$ under 755·5 mm. pressure, and is volatile with steam. The *picrate* crystallises in yellow needles, and melts at $144-145^{\circ}$. The *platinochloride* melts at $188-189^{\circ}$ with decomposition.

Amidoethylic orthotoluate, $\text{C}_6\text{H}_4\text{Me} \cdot \text{COO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$, is obtained by treating the above oxazoline with a molecular proportion of acid; it is a colourless oil. The *hydrobromide* crystallises in colourless tablets, and melts at $155-156^{\circ}$. The *picrate* melts at $187-188^{\circ}$.

Chlorethylorthotoluamide, $\text{C}_2\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_7\text{H}_7$, is obtained by heating the oxazoline with excess of hydrochloric acid on the water-bath. It crystallises in white needles, and melts at $72-73^{\circ}$.

β-Bromopropylorthotoluamide, $\text{CHMeBr} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_7\text{H}_7$, ob-

tained in a similar way to the bromethyl compound, crystallises in colourless needles, and melts at $85-86^{\circ}$.

β -Methylorthotolylloxazoline, $\begin{matrix} \text{CHMe}\cdot\text{O} \\ | \\ \text{CH}_2-\text{N} \end{matrix} \gg \text{C}\cdot\text{C}_7\text{H}_7$, is obtained by heating the preceding compound with alcoholic potash on the water-bath. It is a colourless oil, and boils at $257-258^{\circ}$ under 763 mm. pressure. The *picrate* crystallises in yellow needles, and melts at $123-129^{\circ}$. The *platinochloride* crystallises in rhombic leaflets, and melts at $180-181^{\circ}$. When treated with excess of hydrochloric acid, it yields β -chloropropylorthotoluamide, which crystallises in white needles, and melts at 84° .

β -Amidopropyl orthotoluate hydrobromide is obtained by evaporating an aqueous solution of bromopropyltoluamide. It crystallises in white needles, and melts at $139-140^{\circ}$. The *free base*,



is easily soluble in water. The *picrate* crystallises in yellow plates, and melts at $191-192^{\circ}$. The *platinochloride* melts at $213-214^{\circ}$ with decomposition.

Bromethylparatoluamide, prepared in the same way as the ortho-compound, crystallises in white leaflets, melts at $128-129^{\circ}$, and is very unstable.

μ -Paratolylloxazoline crystallises in beautiful white needles, melts at 66° , boils at $264-265^{\circ}$ under 760.2 mm. pressure, and is volatile with steam. The *picrate* melts at $187-188^{\circ}$. The *platinochloride* crystallises in orange needles, and melts at $185-186^{\circ}$ with decomposition. When evaporated with fuming hydrochloric acid, it yields chlorethylparatoluamide.

Amidoethyl paratoluate hydrobromide is obtained by evaporating bromethylparatoluamide with water. It crystallises in rhombic tablets, and melts at 167° . The *picrate* crystallises in yellow needles, and melts at $179-180^{\circ}$.

β -Bromopropylparatoluamide is very unstable and easily goes over into the oxazoline. It crystallises from light petroleum in needles, begins to melt at 74° , then solidifies, and melts again at $157-158^{\circ}$.

β -Methylparatolylloxazoline is an oil, and boils at $264-265^{\circ}$ under 754 mm. pressure. The *picrate* melts at $182-183^{\circ}$. The *platinochloride* crystallises in flat, orange leaflets, and melts at $183-184^{\circ}$ with decomposition. When evaporated with fuming hydrochloric acid, it yields β -chloropropylparatoluamide, which crystallises in white needles, and melts at $77-78^{\circ}$.

Thiazolines are obtained by heating molecular proportions of phosphorus pentasulphide and the acidyl derivatives of brominated amines at 150° in an oil-bath.

β -Methylorthotolylthiazoline is an oil which boils at $284-295^{\circ}$ under 753.5 mm. pressure; it is volatile with steam, and has an odour resembling that of quinoline. The *picrate* crystallises in yellow needles, and melts at $135-136^{\circ}$.

β -Methylparatolylthiazoline is a pale-yellow oil, and distils at $294-295^{\circ}$ under 757.5 mm. pressure. The *picrate* crystallises in

yellow needles and melts at 140—141°. The *platinochloride* melts at 175—176° with decomposition.

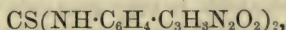
The author has also prepared methyl- μ -phenylthiazoline, ortho- and para-tolylthiazoline, which have been previously described by Gabriel and Heymann (Abstr., 1891, 701). Methyl- μ -phenylthiazoline picrate prepared by this method melts at 156—157°; when prepared by Gabriel's method, it melts at 154°. Orthotolylthiazoline, contrary to the statement of Gabriel and Heymann, distils without decomposition at 281—282° under 760.5 mm. pressure. E. C. R.

Paranitrophenylmethyloxybiazalone and its Decomposition Products. By M. FREUND and H. HAASE (*Ber.*, 26, 1315—1321).—Phenylmethyloxybiazalone yields a mono- and a di-nitro-derivative. The mononitro-derivative contains the nitro-group in the para-position; since, when treated with alcoholic potash, it yields acetylparanitrophenylhydrazine, and this, when boiled with dilute hydrochloric acid, is converted into paranitrophenylhydrazine.

Dinitrophenylmethyloxybiazalone, $C_6H_3(NO_2)_2 \cdot C_3H_3N_2O_2$, is obtained by gradually adding fuming nitric acid to phenylmethyloxybiazalone dissolved in concentrated sulphuric acid. It melts at 127°, and closely resembles the mononitro-compound.

Paramidophenylmethyloxybiazalone, $NH_2 \cdot C_6H_4 \cdot C_3H_3N_2O_2$, is obtained, together with paraphenylenediamine hydrochloride, by warming nitrobiazalone with tin and hydrochloric acid. It crystallises in colourless needles, and melts at 125°. The *hydrochloride* crystallises in leaflets, and melts at 220°. The *platinochloride* crystallises in golden prisms, and does melt at the boiling point of sulphuric acid. The *sulphate* decomposes at 250°. The *nitrate* melts at 180°. The *acetyl* compound crystallises in colourless needles, and melts at 194°. The *benzoyl* compound crystallises in colourless tablets, and melts at 207—208°.

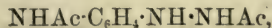
Diparaphenylmethyloxybiazolonethiocarbamide,



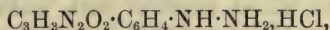
is obtained by the action of carbon bisulphide on an alcoholic solution of the base containing potassium hydroxide. It crystallises in yellow leaflets, and melts at 208°.

Monoparaphenylmethyloxybiazolonethiocarbamide, obtained by boiling the hydrochloride of the base with ammonium thiocyanate, crystallises in needles, and melts at 203°. *Paraphenylmethyloxybiazolonecarbamide*, $NH_2 \cdot CO \cdot NH \cdot C_6H_4 \cdot C_3H_3N_2O_2$, melts at 193°. *Diparaphenylmethyloxybiazolonecarbamide*, $CO(NH \cdot C_6H_4 \cdot C_3H_3N_2O_2)_2$, melts at 290°. *Phenylparaphenylmethyloxybiazolonethiocarbamide* melts at 170°.

Paramidoacetylphenylhydrazine, $NH_2 \cdot C_6H_4 \cdot NH \cdot NHAc$, is obtained by boiling amidophenylmethyloxybiazalone with an aqueous solution of barium hydroxide in the absence of air. It crystallises in colourless leaflets, and melts at 146°. The *acetyl* compound,



crystallises in brownish needles, and melts at 221°.

Parahydrazidophenylmethyloxybiazolone hydrochloride,

is obtained by diazotising the amidobiazolone, pouring the product into a concentrated solution of sodium sulphite, and warming the mixture with zinc-dust and acetic acid until it is colourless. It crystallises in colourless leaflets, and melts at 220° . E. C. R.

Xanthine Derivatives. By P. BALKE (*J. pr. Chem.* [2], 47, 537—567).—The behaviour of the xanthine derivatives with Fehling's solution in the presence of hydroxylamine hydrochloride, as a reducing agent, has been examined. The precipitates obtained in this way with guanine and xanthine are at first white, but speedily become green by oxidation, so that when analysed they show a composition intermediate between a cuprous oxide and a cupric oxide compound. There is sufficient evidence, however, to justify the view that the white precipitate is a compound of equal molecular proportions of the base and cuprous oxide. Heteroxanthine and paraxanthine, prepared from urine by Salomon's process, detailed in the paper, give similar white precipitates. Theobromine and caffeine are the only known xanthine derivatives which do not give precipitates by the above reaction. The uric acid precipitate, $\text{C}_5\text{H}_4\text{N}_4\text{O}_3 \cdot \text{Cu}_2\text{O}$, is yellowish-white at first, but speedily becomes greenish; the carmine precipitate, $\text{C}_7\text{H}_8\text{N}_4\text{O}_3 \cdot \text{Cu}_2\text{O}$, is liable to be mixed with uncombined cuprous oxide which colours it yellow. The adenine and hypoxanthine precipitates are white.

The author proposes to take advantage of the great insolubility of these cuprous oxide compounds for the titration of xanthine derivatives, as has, indeed, been already done for the titration of uric acid. To an alkaline solution of the xanthine derivative, a few cubic centimetres of a solution of hydroxylamine hydrochloride are added, and then Fehling's solution is run in gradually from a burette, the liquid being constantly agitated until the yellow or yellowish-red colour of cuprous oxide makes its appearance, indicating that all the xanthine derivatives have been precipitated. A short interval should be allowed to elapse between each addition of the Fehling's solution, as the separation of the precipitate (or of cuprous oxide) is not very rapid. The results are calculated on the basis that 1 mol. of the derivative is equivalent to 2 atoms of copper; they are not trustworthy for solutions containing less than 1 per cent.

As a means of separating the xanthine derivatives from flesh, the production of the cuprous oxide precipitate compares very favourably with Neubauer's method; a description of how it may be applied is given. A process is also described for extracting the xanthine derivatives from plants, particularly malt sprouts, by means of this reaction.

The reason why very small quantities of sugar in urine are liable to escape detection by the reduction test is the fact that as soon as the cuprous oxide is produced in the hot liquid it combines with xanthine derivatives present, and is no longer recognisable as cuprous oxide.

Protamine, the base isolated by Miescher (this Journal, 1874, 794: 1875, 566), gives the biuret reaction with sodium hydroxide and copper sulphate, but, in the presence of hydroxylamine hydrochloride, a yellow precipitate is obtained which has all the characteristics of a cuprous oxide compound, and yields the original base when treated with hydrogen sulphide. It must be admitted, therefore, that protamine is an individual compound.

The *monosodium derivative* of xanthine, $C_5H_3N_4O_2Na + H_2O$, crystallises in microscopic needles from a solution of the base in the smallest possible quantity of sodium hydroxide. Like monosodium urate, it is decomposed by repeated recrystallisation, and retains its water of crystallisation at a high temperature (190—200°). The author discusses the position of the sodium in the molecule, and is still engaged in the investigation of the action of methylic iodide on the compound.

Episarkine, $C_4H_6N_3O$, is a new base obtained, together with hypoxanthine, when extracting the latter from urine by Salomon's method; it crystallises in prismatic needles, and is less soluble than hypoxanthine, from which it is best separated by dissolving the mixture in as dilute ammonia as possible and saturating the solution with carbonic anhydride, whereon the new base crystallises out. The yield was 0.4 gram from 1600 litres of urine. When evaporated with nitric acid and chlorine, the base remains white, and is not changed by ammonia; when evaporated with concentrated hydrochloric acid and potassium chlorate, a white residue is obtained which becomes intensely violet in an atmosphere of ammonia. One part of episarkine dissolves in 13,000 parts of cold water (no temperature given). The *hydrochloride* crystallises readily, in needles, from a hydrochloric acid solution of the base. No insoluble sodium derivative was obtained. With silver nitrate, the base gives a white precipitate insoluble in nitric acid, but soluble in ammonia. White precipitates were obtained with phosphotungstic acid, mercuric chloride, and ammoniacal lead acetate. The base resembles adenine, except in its great insolubility in cold water.

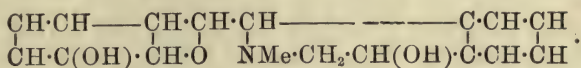
The paper concludes with a table exhibiting the reactions of the xanthine derivatives.

A. G. B.

Constitution of Morphine. By G. N. Vis (*J. pr. Chem.* [2], 47, 584—591; compare Knorr, Abstr., 1889, 905).—The author summarises the known facts with regard to morphine, and the conclusions to be drawn from them, as follows:—(1.) The nitrogen atom in morphine has a methyl group attached to it (Abstr., 1889, 417). (2.) Morphine is a tertiary base. (3.) Morphine yields pyridine in several reactions, and, therefore, probably contains a pyridine ring (compare Knorr, *loc. cit.*). (4.) Morphine derivatives easily pass into phenanthrene derivatives (Abstr., 1882, 1112; *loc. cit.*), indicating either the presence of a phenanthrene nucleus or an unusual predisposition for the production of one. (5.) By suitable oxidation, morphine yields picric acid, and by fusion with caustic alkali, protocatechuic acid; both reactions indicate a benzene ring, and the latter suggests analogy of constitution with that of papaverine, which so readily yields proto-

catechuic acid. (6.) Morphine contains two hydroxyl groups (Abstr., 1884, 615), one of which has phenolic functions, the other alcoholic functions. The third oxygen atom in morphine is indifferent, and apparently of an ethereal nature. (7.) The hydroxyl group which is apparently alcoholic retains its character in methylmorphimethine (Abstr., 1889, 417), and also, it would seem, in the hydroxyethyl-dimethylamine.

Ill-content with Knorr's formula for morphine (Abstr., 1889, 905), the author suggests the following as being in accord with the above facts:—



He proceeds to explain the decomposition of methylmorphimethine into hydroxyethyl-dimethylamine and hydroxymethoxyphenanthrene in the light of this formula, and proposes structural formulæ for pseudo- and apo-morphine.

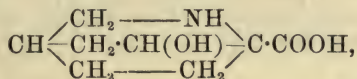
A. G. B.

Formula of Tropine. By J. F. EYKMAN (*Ber.*, 26, 1400—1403).—By comparison of the molecular refraction of tropine and pseudo-tropine with that of certain substances of, in some respects, similar constitution, the conclusion is drawn that these two compounds do not, as Ladenburg thinks (this vol., i, 426), contain a double bond.

C. F. B.

nor.-r-Ecgonine. By A. EINHORN and A. FRIEDLAENDER (*Ber.*, 26, 1482—1491).—In this paper, the constitutional formulæ adopted are based on those proposed by Merlin.

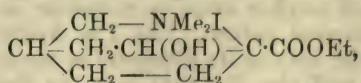
When *r*-ecgonine hydrochloride is oxidised with alkaline permanganate solution at 0°, and the crude product boiled with sulphuric acid and absolute alcohol, *ethylic nor.-r-ecgonine*, which crystallises in colourless, transparent needles, and melts at 137°, is obtained; the *methyl*ic salt melts at 160°. *Nor.-r-ecgonine*,



is obtained by boiling either of the last-mentioned salts with water in a reflux apparatus for 12 hours; when pure, it crystallises in colourless needles. It is very insoluble in most solvents, its aqueous solution is without action on litmus, and metallic salts could not be obtained, but it forms crystalline salts with acids. *Ethylic nitroso-nor.-r-ecgonine* is an oily compound. The authors also find that the benzoyl derivative of ethylic cocaylhydroxyacetate (Abstr., 1889, 169) yields an oily *nitroso*-compound, and they therefore regard cocaylhydroxyacetic acid as *nor.-l-ecgonine*.

Ethylic benzoyl-nor.-r-ecgonine melts at 127°, and the *platinochloride* melts at 142°. *Benzoyl-nor.-r-ecgonine* is obtained by boiling the ethylic salt with water. Unlike the corresponding derivative of the *l*-series, neither a copper nor a silver salt could be obtained from it.

When ethylic nor.-*r*-ecgonine is dissolved in ethylic acetate and treated with methylic iodide, a *quaternary ammonium iodide*,



melting at 178° is obtained; when an aqueous solution of this is shaken with silver chloride, the *methochloride* is formed as an oil; it yields an *aurochloride* melting at 182°. The methiodide just described seems also to be obtained by the action of methylic iodide on ethylic *r*-ecgonine. When the methiodide from either source is boiled with dilute sodium hydroxide, dimethylamine and an *acid*, $\text{C}_8\text{H}_8\text{O}_2$, melting at 55–56° is obtained. This compound is being further studied; it is also formed in the same manner from the methiodides of methylic *r*-ecgonine, and of ethylic *l*-ecgonine.

The authors have proved the relationship of nor.-*l*-ecgonine to *r*-ecgonine to be that above shown, by the fact that the former is converted into the latter on methylation.

A. R. L.

Ptomaines. By A. GARCIA (*Zeit. physiol. Chem.*, 17, 543–595).—In putrefying mixtures of horseflesh and pancreas, hexamethylenediamine, $\text{C}_6\text{H}_{16}\text{N}_2$, occurs in addition to the diamines already described.

Ptomaines may be best estimated by Baumann's benzoic chloride method. In mixtures, the presence of sugar reduces the formation of diamines to about half; the same diamines are, however, formed.

The production of putrescine, cadaverine, and hexamethylenediamine is an early phenomenon in such putrefying mixtures at a favourable temperature; it reaches its highest point within about three days, and they are produced in the same proportion throughout. In cystinuria, tetramethylenediamine only is produced in the later stages. Feeding on cheese causes an increase, on carbohydrate a diminution, in diamine production. Infection of nutritive media with the fæces of such patients causes the appearance of ptomaines. In media not so infected, exclusion of air hinders the formation of diamines during the first few days (four days in the experiments which are described).

W. D. H.

Urobilin. By A. EICKHÖLZ (*J. physiol.*, 14, 326–339).—Normal urobilin exists in the urine totally or partially as chromogen, and can by appropriate methods be isolated so as to furnish a solution containing the pigment wholly or partly as chromogen. Urobilin and urochromogen are not highly coloured, and the urine cannot depend on them to any great extent for its colour. Pathological urine contains an additional pigment, *pathological urobilin* with a different absorption spectrum; it also can be isolated as a chromogen. Both urobilins can be reduced by sodium amalgam, but the reduction product differs from urochromogen, and may be termed *urobilinogen*. On prolonged reduction, bilirubin furnishes a substance resembling urobilin. Maly's hydrobilirubin is an intermediate product in the reduction. Hæmatin in acid solution is reduced to a substance closely

resembling urobilin. Incomplete reduction furnishes a substance also resembling urobilin, but which immediately reverts to the state of urohæmatoporphyrin on standing.

W. D. H.

Urinary Colouring Matters. By H. ROSIN (*Chem. Centr.*, 1893, i, 487—488; from *Deut. Med. Woch.*, 19, 51—54).—The red colouring matter obtained in Rosenbach's reaction can not only be isolated in the crystalline form from urine, but also from the vegetable organism (and from indigo-blue). It is named by the author indigo-red.

When urine is heated with nitric acid, a reddish coloration is produced; this has been observed, in the case of pathological urine, by Nencki and Sieber. The colouring matter is obtained by heating urine, previously decolorised with basic lead acetate or animal charcoal, with an acid and an oxidising agent. Nitric acid alone (not chromic acid) can be used, or hydrochloric or sulphuric acid in the presence of hypochlorite, avoiding an excess of the latter. It is soluble in amyl alcohol, but insoluble in ether, chloroform, and benzene. It has acidic properties, and exhibits a characteristic absorption spectrum which is identical with that observed by Nencki and Sieber for urorosein. The colouring matter occurs in larger quantity in pathological than in normal urine.

In order to obtain the substance from which the colouring matter is produced, ox-urine is precipitated with basic lead acetate and the filtrate treated with ammonia; the precipitate is collected, dried at 70°, extracted with absolute alcohol, the lead removed from the alcoholic solution by hydrogen sulphide, and the filtrate concentrated and fractionally precipitated with ether. The chromogen crystallises from the ethereal alcoholic solution in colourless, transparent needles soluble in water.

A. R. L.

Vegetable Nuclein. By P. PETIT (*Compt. rend.*, 116, 995—997).—Malt combs (Touraillons) containing a large proportion of germs mixed with radicles are heated at 60° for some minutes with a 1 per cent. solution of potassium hydroxide. The liquid is filtered, allowed to cool, and exactly neutralised with dilute hydrochloric acid, when a greyish precipitate forms and rapidly agglomerates. It is washed with water, then with alcohol and ether, and is dried over sulphuric acid. It forms brown-black fragments with a conchoidal fracture, and has the composition C, 43.18; H, 6.64; N, 12.86; P, 1.11; Fe, 0.195; ash, 6.2; SiO₂, 3.2; O, 31.1 = 100. Unlike the animal nucleins, described by Kossel, Liebermann, and others, it contains no sulphur.

When placed in solutions of sodium chloride, vegetable nuclein swells up and becomes greyish; it gives no reaction with Millon's reagent, but is dissolved by alkalis. When mixed with ammoniacal potassium ferrocyanide and then with excess of acetic acid, it yields a white precipitate which gradually becomes blue, the change being more rapid the more concentrated the acid and the higher the temperature. With hydrochloric acid, the change to blue is almost instantaneous. Tannin gives a white precipitate which blackens on heating. The two last reactions are regarded by Bunge as general for all nucleins.

When the nucleïn from barley is heated with water under a pressure of 4 atmos., it dissolves and yields a pale-yellow solution on which *Aspergillus* or *Penicillium* grows with extreme rapidity.

The solution gives with ferrocyanides and with tannin the same reactions as the original compound, but it is not precipitated by acids. With ammoniacal silver nitrate it yields a grey precipitate which blackens when heated, and with copper sulphate it yields, when heated, an amorphous, grey precipitate. When boiled for a long time with nitric acid, it dissolves completely, and yields oxalic acid and an acid that forms a crystalline compound with phenylhydrazine.

Vegetable nucleïn is absorbed by many plants, and particularly by barley. A solution of it seems to be a particularly advantageous means of supplying to barley the iron that is indispensable for its proper development.

C. H. B.

The Filtration of Caseïn Solutions through Porcelain. By L. HUGOUNENQ (*Ann. Chim. Phys.* [6], 28, 528—537).—Porcelain filters allow albuminous substances to pass through them very unequally; asbestos porcelain is traversed more easily than the biscuit of the Chamberland tubular filters. Some proteïds leave a residue on the exterior surface of the filter which never passes through; a small quantity remains fixed in the pores of the septum and resists washing with water. In the estimation of proteïds, 12—15 per cent. loss may occur in this way. The filtration of certain albuminous substances through porcelain is accompanied by chemical changes. Gas is evolved, and caseïn, precipitable by acetic acid, passes through to the extent of one-third its total amount. The asbestos or ordinary porcelain filters only allow the precipitable caseïn to pass through when the alkalinity of the solution corresponds with a value requiring 1.5 grams of sulphuric acid per litre to neutralise it, and even then a considerable residue remains behind; this can only be avoided by rendering the solution more strongly alkaline. The chemical composition of a culture medium containing proteïds gives no indication as to its chemical composition after sterilisation by means of the tubular filter.

A. R. L.

Organic Chemistry.

Action of Mineral Acids on Dimethylallene. By I. KONDAKOFF (*J. Russ. Chem. Soc.*, **24**, 513—515).—The author showed (*J. Russ. Chem. Soc.*, **21**, 36) that fuming hydrochloric acid acted on dimethylallene with formation of the unsaturated chloro-derivative, $\text{CMe}_2\text{Cl}\cdot\text{CH}:\text{CH}_2$, and of a saturated dichloro-derivative to which he attributed the constitution $\text{CMe}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$. He now proves the correctness of the last formula by preparing the corresponding glycol by heating the dichloride for 20 hours with aqueous potash. The glycol, $\text{C}_5\text{H}_{10}(\text{OH})_2$, is a syrup having the sp. gr. 0.9951 at 0° and 0.9892 at 20° . It has a caustic, cooling taste, and boils at $202\text{--}203^\circ$. On oxidation with 1 per cent. potassium permanganate solution, it yields β -hydroxyvaleric acid, with traces of glyoxylic, acetic, and formic acids.
J. W.

Cyanogen. By T. ZETTEL (*Monatsh.*, **14**, 223—232).—The products of decomposition of this substance have again been studied, and, in the main, the results of previous observers have been confirmed. When solutions of cyanogen in acetic acid or dilute acetic, hydrochloric, or sulphuric acids are allowed to remain at the ordinary temperature, no change takes place. A solution in concentrated hydrochloric acid, when kept at the ordinary temperature, yields, chiefly, oxamide, together with some ammonia and oxalic acid, whilst a solution in dilute hydrochloric acid (one-fifth), heated for six hours at 150° , gives oxalic acid, ammonia, and some carbonic anhydride. A solution in 10 per cent. aqueous potash decomposes at the ordinary temperature, yielding azulmic, hydrocyanic, and isocyanic acids, together with ammonia and carbonic acid, but no oxalic acid. An aqueous solution yields at the ordinary temperature, or more quickly at 100° , azulmic acid, oxalic acid, ammonia, carbonic anhydride, hydrocyanic acid, and carbamide.
C. F. B.

Hydrolysis of Aromatic Nitriles. By L. BOUVEAULT (*Bull. Soc. Chim.* [3], **9**, 368—373).—The process consists in converting the nitrile into the corresponding amide by digesting it with 85 per cent. sulphuric acid (or 90 per cent. if it be insoluble in acid of 85 per cent. strength) at 100° , dissolving the amide in cold, strong sulphuric acid and adding a concentrated aqueous solution of the calculated quantity of sodium nitrite, in such manner that the temperature shall not rise above $30\text{--}40^\circ$; a few moments at a temperature of $40\text{--}50^\circ$ will complete the quantitative conversion of the amide into the acid.

A. G. B.

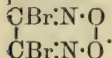
Sodium Platinocyanide. By T. WILM (*Zeit. anorg. Chem.*, **4**, 298—299; compare Abstr., 1886, 604).—This salt may readily be prepared from the mother liquor of a preparation of the potassium salt by precipitating as copper platinocyanide and heating this with a slight excess of soda solution. It crystallises with $3\text{H}_2\text{O}$ in long,

lustrous, colourless, transparent prisms or needles. These are stable in the air, and become anhydrous at 120—125°. The crystals do not fluoresce like those of the potassium salt, nor are they altered by chlorine under the same conditions as those under which the chlorine compound of the potassium salt is formed (Abstr., 1889, 951).

A. G. B.

Fulminic acid and its Derivatives. By R. SCHOLL (*Chem. Centr.*, 1893, i, 730—731).—The author gives a historical survey of fulminic acid, and discusses the various formulæ which have been suggested for it; he considers, with Steiner, that its properties and modes of formation are best explained on the assumption that it is dioximidoethylene, NOH:C:C:NOH .

Bromonitromethane, $\text{CH}_2\text{Br}\cdot\text{NO}_2$, is formed by the action of cyanogen bromide on sodium nitromethane. Iodoacetoneitrile, $\text{CN}\cdot\text{CH}_2\text{I}$, can be prepared by heating chloroacetoneitrile with potassium iodide and methyl alcohol, and is a colourless, heavy oil, volatile with steam, boiling at 76—77° under a pressure of 12 mm., and at 182—184° with decomposition under 720 mm. pressure; its vapour attacks the eyes, and it produces burns when brought into contact with the skin. By the action of silver nitrite on the preceding compound, two substances are formed; one, $\text{C}_2\text{H}_2\text{N}_2\text{O}$, which is crystalline, melts at 72—73°, and is being further investigated; the second is a colourless, viscid liquid boiling at 160—162° under a pressure of 12 mm. The compound does not appear to have acidic properties, and as on treatment with sodium ethoxide or with benzylamine, a nitro-group is eliminated, it may be represented by the formula $\text{CN}\cdot\text{C}(\text{NO}_2)\cdot\text{NO}\cdot\text{CH}_2\cdot\text{CN}$. Diiodonitroacetoneitrile and dibromonitroacetoneitrile are represented by the formulæ $\text{C}_2\text{N}_2\text{O}_2\text{I}_2$ and $\text{C}_2\text{N}_2\text{O}_2\text{Br}_2$ respectively; the latter does not combine with hydrogen sulphide, and on treatment with hydrochloric acid is resolved into hydrogen bromide, hydroxylamine, oxalic acid, and a little ammonia; it is therefore not a direct substitution product of mercuric fulminate, and probably has the formula



J. B. T.

Normal Amyl Alcohol. By L. TISSIER (*Bull. Soc. Chim.* [3], 9, 100—101).—Wischnegradski's inference that this alcohol is contained in fermentation amyl alcohol, because the amylene derived from the latter contains symmetrical methylethylethylene, is erroneous, for the author was unable to isolate any of the normal alcohol from 1600 litres of fusel oil. The methylethylethylene was doubtless formed from active amyl alcohol by molecular transformation, and, as an experiment showed, it can actually be obtained in considerable quantity by allowing this alcohol to flow over fused zinc chloride contained in an iron tube.

C. F. B.

Fourth Primary Amylic Alcohol. By L. TISSIER (*Ann. Chim. Phys.* [6], 29, 321—389).—An account of the preparation and properties of the primary amylic alcohol trimethylcarbincarbonol has already been published (Abstr., 1891, 998). In the present

memoir, the author gives his work in detail and describes several new derivatives of trimethylethylic alcohol.

The *glycol*, $\text{CMe}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CMe}_3$, is formed by the action of sodium amalgam on trimethylacetaldehyde; it was also separated from the portion of the reduction product of trimethylacetic chloride (*loc. cit.*) boiling above 180° . It crystallises in tables, melts at $83\text{--}84^\circ$, boils at $185\text{--}187^\circ$, has the odour of pinacone, and is slightly soluble in water; when treated with one equivalent of acetic acid (m. p. $16\cdot6^\circ$), $27\cdot56$ per cent. of the latter is converted into the acetate.

Trimethylethylic chloride is obtained by chlorinating tetramethylmethane; also by saturating trimethylcarbincarbonol cooled below 0° with hydrogen chloride, or by the action of phosphoric chloride on the same alcohol; it is a colourless, mobile liquid of agreeable odour, partially decomposes when distilled, and has a sp. gr. of $0\cdot8792$ at 0° ; an *amylbenzene* boiling at $185\text{--}190^\circ$ is formed when the chloride is treated with benzene and aluminium chloride (compare Schramm, *Abstr.*, 1889, 127). The *bromide*, $\text{CMe}_3\cdot\text{CH}_2\text{Br}$, is a liquid of sp. gr. $1\cdot2253$ at 0° , boils at $108\text{--}109^\circ$, and when heated with alcoholic potash yields *trimethylethylene*, $\text{CMe}_2\cdot\text{CHMe}$, the *dibromide* of which boils at about 175° . The *iodide*, $\text{CMe}_3\cdot\text{CH}_2\text{I}$, has a sp. gr. of $1\cdot0502$ at 0° , and boils at $127\text{--}129^\circ$ with decomposition; the distillate yields an *acetate* boiling at 124° , which on hydrolysis is converted into tertiary amylic alcohol.

Trimethylethylic acetate, $\text{CMe}_3\cdot\text{CH}_2\cdot\text{OAc}$, is a colourless liquid of sp. gr. $0\cdot86453$ at 0° , and boils at 126° ; the *propionate* has a sp. gr. of $0\cdot87327$ at 0° , and boils at $147\text{--}148^\circ$; the *butyrate* has a sp. gr. of $0\cdot87193$ at 0° , and boils at $165\text{--}166^\circ$; the *isobutyrate* has a sp. gr. of $0\cdot86957$ at 0° , and boils at $158\text{--}159^\circ$; the *trimethylacetate* has a sp. gr. of $0\cdot86078$ at 0° , and boils at $162\text{--}164^\circ$; and the *benzoate* boils at $139\text{--}141^\circ$.

When excess of sulphuric acid is added by degrees to trimethylcarbincarbonol, the *amylsulphuric acid* is formed.

Trimethylethylamine, $\text{CMe}_3\cdot\text{CH}_2\cdot\text{NH}_2$, is obtained by reducing an alcoholic solution of trimethylacetonitrile with sodium; it boils at $81\text{--}82^\circ$; the *hydrochloride* is a colourless substance which melts with decomposition at about 85° ; the *platinochloride*, *aurochloride*, and *mercurochloride* were also prepared.

The trimethylacetic acid employed in this research was prepared by the oxidation of pinacolin with potassium dichromate and dilute sulphuric acid. It has, therefore, been necessary to prepare large quantities of pinacone; the method used was the action of sodium on acetone floating on a solution of potassium carbonate, and the author has examined the oily bye-product insoluble in water obtained in the latter reaction. Two compounds were isolated from this bye-product: mesityl oxide (b. p. $130\text{--}132^\circ$), and a compound $\text{C}_9\text{H}_{14}\text{O}$, boiling at $129\text{--}133^\circ$ under a pressure of 4 mm., and at $220\text{--}230^\circ$ with decomposition under the ordinary pressure; the *oxime*, $\text{C}_9\text{H}_{14}\cdot\text{NOH}$, is a colourless, crystalline compound melting at 102° and boiling at $155\text{--}160^\circ$ (4 mm.).

New methods of preparing trimethylacetic chloride, trimethyl acetamide, and trimethylacetonitrile are described.

A. R. L.

Allylmethylethylcarbinol. By N. SAYTZEFF (*J. Russ. Chem. Soc.*, **24**, 468—471).—A mixture of methyl ethyl ketone (300 grams) and allylic iodide (750 grams) was added drop by drop to freshly heated granulated zinc contained in a retort surrounded by ice-cold water; on the following day, the product was decomposed with water and distilled. The oily layer was then separated from the aqueous layer, dried with fused potash, and submitted to fractional distillation, 70 grams of an alcohol boiling between 135° and 145° being obtained. This yielded 20 grams of pure *allylethylmethylcarbinol* boiling at 138·5—139·5° under a pressure of 753 mm. It is a colourless oil having a specific gravity of 0·8586 at 0°/0° and 0·84315 at 20°/20°. Its *acetate* boils at 158—160° and has the sp. gr. 0·8943 at 0°/0°.

The corresponding *glycerol*, $C_7H_{13}(OH)_3$, was obtained by oxidising the carbinol with potassium permanganate, filtering, evaporating on the water-bath, and extracting with alcohol. It is a colourless, viscous liquid, easily soluble in water, alcohol, and ether. The *triacetate* was prepared by heating the glycerol with acetic anhydride for three hours at 120°, and forms a liquid which is soluble with difficulty in water, but dissolves readily in alcohol and ether. J. W.

Allylmethylhexylcarbinol. By A. BOYANUS (*J. Russ. Chem. Soc.*, **24**, 471—473).—Allylmethylhexylcarbinol was prepared from methyl hexyl ketone (98 grams) and allylic iodide (130 grams) by the action of zinc (compare preceding abstract). The portion of the resulting oil that boiled at 215—216° was the required product. On oxidation with permanganate, it yielded the *glycerol*, $C_{11}H_{21}(OH)_3$, which, on treatment with acetic anhydride, was converted into the triacetate, $C_{11}H_{21}(OAc)_3$. J. W.

Action of Acetic Anhydride on Linalol. By G. BOUCHARDAT (*Compt. rend.*, **116**, 1253—1255).—Linalol obtained from *Lavandula spica* seems to be identical with licareol (this vol., i, 493 and 495). When treated with acetic anhydride at the ordinary temperature, it yields an acetate which regenerates linalol on saponification, but if heated at 100—120° a different acetate is formed, which, when saponified, yields a new alcohol, analogous to or identical with licarhodol. This acetate boils at 120—125°, under a pressure of 25 mm., and is optically inactive; sp. gr. at 0° = 0·9377—0·9467. When saponified with alcoholic potash at 100°, it yields a neutral compound $C_{10}H_{16}O$, which, under normal pressure, boils at 226—231° with slight decomposition; sp. gr. at 0° = 0·9061; it has an odour of roses, is optically inactive, combines readily with bromine, and yields an inactive dihydrochloride of sp. gr. 1·046. This alcohol, and therefore licarhodol also, seems to be identical with the geraniol obtained from Indian essential oil of geranium. C. H. B.

¶ **Licarhodol from Licareol.** By C. BARBIER (*Compt. rend.*, **116**, 1200—1202).—The acetate which is obtained, together with licarene, by the action of acetic anhydride on licareol, can readily be purified by fractionation under low pressure. It has the empirical formula $C_9H_{15}\cdot CH_2\cdot OAc$, and is a colourless liquid with a strong odour of

angelica. It boils at 135° under a pressure of 21.5 mm.; sp. gr. at $0^{\circ} = 0.9298$; refractive index at 19.5° for $\lambda 645 = 1.4594$, and for $\lambda 452.6 = 1.4734$. It acts feebly on polarised light, a column 200 mm. in length giving a rotation of $-0^{\circ} 32'$. The acetate is insoluble in water; it is rapidly saponified by alcoholic potash, and yields a new alcohol, *licarhodol*.

Licarhol has the same composition, $C_{10}H_{18}O$, as licareol, but differs from it markedly in physical properties. It is a colourless, oily liquid, with a strong odour of roses, and is insoluble in water. It boils at 122° under a pressure of 19 mm.; sp. gr. at $0^{\circ} = 0.8952$; refractive index at 15.3° for $\lambda 645 = 1.4740$, and for $\lambda 452.6 = 1.4893$; rotatory power of a column 200 mm. long $= -1^{\circ} 14'$ at 20.4° .

When oxidised, licarhodol yields an aldehyde identical with that obtained from licareol, and when it is treated with energetic oxidising agents, the products are the same as from licareol. With dry hydrogen chloride, it yields a dihydrochloride, $C_{10}H_{18}Cl_2$, identical with the dihydrochloride of licarene.

It follows that licarhodol is a stable stereoisomeride of licareol, the two being distinguished by their behaviour with acetic anhydride. This result confirms the constitution previously attributed to licareol. (See this vol., i, 495, 496.)

C. H. B.

Ethylmethylpropylethylene Glycol. By I. PANFILOFF (*J. Russ. Chem. Soc.*, 24, 473—477).—Methyldipropylcarbinol, boiling at 159 — 161° , was saturated in the cold with hydrogen chloride, allowed to remain for 24 hours, and then poured into cold water. From 58.5 grams of alcohol there were obtained in this way 66 grams of the corresponding chloride, which was then dropped into a solution of 75 grams of potash in 150 grams of alcohol heated on the water-bath. The heating was continued for four hours, the mixture then being distilled almost to dryness. On treating the distillate with water, about 45 grams of an oily product were obtained, which, on fractionation, gave 28.5 grams of a hydrocarbon, C_8H_{16} , boiling between 118° and 121° . This hydrocarbon (20 grams) was oxidised in the cold with 1 per cent. potassium permanganate solution, the product distilled with steam, whereby half the original octylene was recovered, filtered, neutralised with sulphuric acid, and distilled to a small bulk. From the second distillate 10 grams of a viscid liquid was extracted with ether, and this on fractionation gave 4 grams of a substance, $C_8H_{16}(OH)_2$, boiling between 210° and 215° . Propionic and acetic acids were also found in the oxidation product. As Sokoloff has shown the hydrocarbon C_8H_{16} to be $CMePr \cdot CHEt$, the glycol must have the constitution $CMePr(OH) \cdot CHEt(OH)$.

J. W.

Birotation of Glucose. By B. TOLLENS (*Ber.*, 26, 1799—1802).—In a recent paper (*Bull. Soc. Chim.* [3], 9, 401, 511), Béchamp ascribes the property of birotation shown by solutions of glucose to the fact that in the freshly prepared solutions the sugar is present as hydrate, and that the hydrate gradually dissociates, until, after 24 hours, it is all present in the form of anhydrous glucose. The author has long been engaged on experiments with the view of ascertaining the

cause of the birotation, and has come to a conclusion identical with that of Béchamp. He has found that anhydrous glucose dissolves in water and in dilute ammonia with absorption of heat in the first instance, but in the case of the aqueous solution a rise of temperature quickly follows, and the solution shows the double rotatory power, which then gradually diminishes. No subsequent evolution of heat occurs with the ammonia solution, and the latter has the rotatory power shown by the aqueous solution after 24 hours. It follows, therefore, that the sugar which gives the double rotation is the hydrate, and that this gradually loses water on remaining, re-forming the anhydride. H. G. C.

Decomposition of Galactose by Calcium Hydroxide. By H. KILIANI and H. SANDA (*Ber.*, 26, 1649—1655).—The product obtained by the decomposition of glucoses by caustic alkalis or alkaline earths consists of about 14 per cent. of a saccharine, 41 per cent. of lactic acid, and a residue of about 50 per cent., the nature of which is unknown. In attempting to determine the composition of this residue, the authors have discovered an easy method of preparing metasaccharin and a new saccharin, which they name *parasaccharin*.

Galactose (1 part) is dissolved in water (10 parts), calcium hydrate (0.5 part) added, and the mixture allowed to remain four weeks in a tightly closed flask, when it is filtered, and the filtrate heated to boiling for three hours. It is then saturated with carbonic anhydride, again filtered, concentrated, and allowed to crystallise in a cool place. In about 10 days, 14 per cent. of calcium saccharinate separates out. The authors were unable to obtain metasaccharin by boiling a solution of galactose with lime. On concentrating the solution of calcium salts, they were unable to obtain the smallest trace of calcium isosaccharinate (Cuisinier, *Mon. Sci.*, 1882, 521).

The mother liquors of the calcium metasaccharinate were precipitated with oxalic acid, and extracted with ether. In this way an acid syrup, insoluble in ether, was obtained, which when partially neutralised with barium carbonate and mixed with alcohol, yielded a crystalline barium salt, containing a new saccharinic acid mixed with some barium metasaccharinate. The latter is separated as follows: the barium salts are decomposed with sulphuric acid, the solution evaporated to a syrup and mixed with alcohol, when metasaccharin separates. By converting the uncrystallisable residue into calcium salt and adding alcohol, the last traces of calcium metasaccharinate crystallise out.

Parasaccharin has almost the same rotatory power as metasaccharin. Under the same conditions metasaccharin gave $[\alpha]_D = -27.7^\circ$, parasaccharin $[\alpha]_D = -26.1^\circ$. The barium salts cannot be distinguished from each other. Calcium parasaccharinate, however, does not crystallise, whereas the calcium metasaccharinate crystallises very readily. Moreover, parasaccharinic acid does not yield a crystalline phenylhydrazide.

When the syrup obtained by decomposing pure barium parasaccharinate with sulphuric acid is boiled with hydriodic acid, α -ethylbutyrolactone is obtained. When parasaccharinic acid is heated

with silver oxide, it yields carbonic anhydride, glycollic acid, and a small quantity of an intermediate compound. E. C. R.

Absence of Spontaneous Inversion of Cane Sugar in Aqueous Solution at the Ordinary Temperature, and the Cause of its Apparently Spontaneous Inversion under the Action of Light.

By A. BÉCHAMP (*Bull. Soc. Chim.* [3], 9, 21—27).—In every case where the author found that inversion of cane sugar had taken place, organisms were present. The organisms concerned in the inversion are not entirely destroyed by boiling the solutions nor even by the addition of phenol. Ordinary white loaf sugar gives solutions which show greater inversion than solutions of the purest sugar-candy similarly treated, owing to the small quantities of proteid and mineral matters contained in the former favouring the growth of the organisms. The exposure to sunlight of sealed tubes containing samples simply favours the growth of the organisms by raising the temperature of the containing solution. W. T.

Recent Investigations on Carbohydrates. By W. E. STONE (*Chem. News*, 67, 304—306).—A valuable *résumé* of the work in this subject during the past year.

Metaldehyde. By C. FRIEDEL (*Bull. Soc. Chim.* [3], 9, 384—385).—Tröger (this vol., i, 64) has observed the transformation of a sample of metaldehyde into paraldehyde. The author finds that when dry metaldehyde is heated in a sealed tube at 60—65° for some hours, it becomes converted into a mixture of paraldehyde with a little aldehyde. Recent work having shown that metaldehyde has the same molecular weight as paraldehyde, the author thinks that this new observation furnishes evidence that these two compounds are stereoisomerides, which may be represented by a triangle with the carbon atoms of the CHO groups of the three aldehyde molecules at its three angles, united in each case by an oxygen atom. The meta- and para-compounds will thus be *cis*- and *trans*-derivatives, according as the methyl groups are on one or other of the sides of the plane of the triangle. A. G. B.

Action of Sulphuric acid on the Pinacone of Methyl Ethyl Ketone. By P. HERSCHMANN (*Monatsh.*, 14, 233—244).—When this pinacone, $\text{OH} \cdot \text{CMeEt} \cdot \text{CMeEt} \cdot \text{OH}$, is treated with concentrated sulphuric acid, the temperature being kept low, the pinacolone, $\text{CEtO} \cdot \text{CMe}_2\text{Et}$, boiling at 148—153°, is practically the sole product of the reaction. But if the pinacone is boiled with dilute sulphuric acid, then, in addition to the above-mentioned pinacolone, there is obtained a hydrocarbon, C_8H_{14} , boiling at 117—121°, which unites with four atoms of bromine, and seems to polymerise on standing, and also a substance boiling at 132—139°, which is probably the isomeric pinacolone $\text{CMeO} \cdot \text{CMeEt}_2$. C. F. B.

Solubility of Barium and Calcium Butyrate. By A. DESZÁTHY (*Monatsh.*, 14, 245—254).—The solubility of the salts $(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ba}$

+ $2\text{H}_2\text{O}$ and $(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca} + \text{H}_2\text{O}$ in water at various temperatures was determined by shaking the salt with water in an air-bath for $1\frac{1}{2}$ —2 hours, filtering the solution at the same temperature (by means of an arrangement described in detail), and estimating as sulphate the metal in the weighed filtrate. The numbers below give the parts of anhydrous salt which dissolve in 100 parts of water at the temperature indicated.

	0°.	10°.	20°.	30°.	40°.	50.	60°.
Ba salt....	37·42	36·65	36·12	35·85	35·82	36·44	37·68
Ca salt....	20·31	19·05	17·97	17·07	16·35	15·81	15·44
			70°.	80°.	118°.	127°.	
Ba salt.....			39·58	42·13	—	—	
Ca salt.....			15·34	15·34	18·12	19·83	

C. F. B.

Solubility of the Lead Salts of Stearic and Palmitic acids in Ether. By A. LIDOFF (*J. Russ. Chem. Soc.*, **24**, 524—526).—50 c.c. of anhydrous ether dissolves at the ordinary temperature 0·0074 gram of lead stearate (m. p. 122°) and 0·0092 gram of lead palmitate (m. p. 112°).

J. W.

Behenic Acid. By Z. TALANTZEFF (*J. Russ. Chem. Soc.*, **24**, 502—504).—The author prepared behenic acid from iodobehenic acid (obtained by the addition of hydrogen iodide to erucic acid) by reduction in alcoholic solution with zinc and hydrochloric acid. The acid was purified by repeated recrystallisation from alcohol. In a capillary tube, it melted at 84° and solidified at 77 — 79° ; when the thermometer was immersed in a mass of the acid, the melting point was 83° and the freezing point 79° . 100 parts of alcohol (30° Tralles) dissolve 0·102 part of behenic acid, whilst 100 parts of ether at 16° dissolve 1·922 parts of acid.

J. W.

The Wax of Gum-lac. By A. GASCARD (*J. Pharm.* [5], **27**, 365—372).—Gum-lac may be separated into three fractions, respectively insoluble, soluble on boiling, and soluble in the cold in 95 per cent. alcohol. The first contains, besides remains of insects and some nitrogenous substance, a small quantity of a wax melting at 92° ; this is myricyl melissate, $\text{C}_{29}\text{H}_{59}\cdot\text{COOC}_{30}\text{H}_{61}$, and the myricyl alcohol obtained from it by hydrolysis is identical with that from carnauba wax and from beeswax, and melts at 88° , and not at 85° as Brodie stated. The second fraction, soluble in hot alcohol, contains rather more than 50 per cent. of free myricyl alcohol, and yielded on hydrolysis myricyl and a little ceryl alcohol, and palmitic, melissic, oleic, and a little cerotic acid, together with some resinous acids having an aromatic odour.

C. F. B.

New Method of preparing Acrylic acid. By C. MOUREU (*Bull. Soc. Chim.* [3], **9**, 386—392).—Acrylic acid is best prepared by heating β -chloropropionic acid (1 mol.) with aqueous potash (over 2 mols.) in a reflux apparatus, the bulk of the liquid being about

1500 c.c. The acrylic acid is liberated by dilute sulphuric acid and distilled over.

Acrylic chloride is prepared by treating sodium acrylate with phosphoryl chloride. It is a colourless, fuming, acrid liquid, and boils at 75—76° at normal pressure; its sp. gr. at 0° is 1.14; water decomposes it easily, and it undergoes spontaneous alteration, of an undetermined nature, in course of time. By treatment with bromine in chloroform, it yields $\alpha\beta$ -dibromopropionic chloride, which is a heavy, colourless liquid and boils at 191—193° with slight decomposition; its sp. gr. is 2.181 at 0°; it slowly becomes yellow, a change which occurs more rapidly in sunlight.

A. G. B.

Oxidation of β -Chlorcrotonic acids. By I. KONDAKOFF (*J. Russ. Chem. Soc.*, **24**, 508—513).— β -Chlorcrotonic acid (6 grams), when oxidised with 18 grams of potassium permanganate in 1 per cent. solution, yielded acetic acid (3.4 grams) and oxalic acid (1 gram). β -Chlorisocrotonic acid (10 grams), under the same conditions, also gave acetic acid (5 grams) and oxalic acid. No trace of an aldehyde was observed in either case when an insufficient quantity of permanganate was employed. These results are equally well explained, whether we assume crotonic and isocrotonic acids to be geometrically isomeric or not.

J. W.

Action of Sodium Hydrogen Sulphite and of Sulphurous acid on Oleic and Erucic acids. By M. C. SAYTZEFF and A. SAYTZEFF (*J. Russ. Chem. Soc.*, **24**, 477—486).—Oleic acid was heated with an equal weight of a saturated solution of sodium hydrogen sulphite for 10 hours at 175—180°. On cooling, the upper fatty layer crystallised to an easily fusible mass, which was purified by recrystallisation from 90 per cent. alcohol, and finally from ether. The pure substance melted in a capillary tube at 51—52°, and solidified at 40—45° when the thermometer was immersed in the fused substance. Analysis gave numbers agreeing with the formula $C_{18}H_{34}O_2$, and a study of the salts and oxidation products showed that the substance was elaidic acid. The same acid is formed from oleic acid by heating with sulphurous acid for 24 hours at 200°. Erucic acid when treated in the same way yields brassidic acid.

The authors explain the mechanism of the isomeric transformation by assuming the addition of $H\cdot SO_2OH$, rotation into the most favoured position, and subsequent removal of $H\cdot SO_2OH$.

J. W.

Isoerucic acid. By P. ALEXANDROFF and N. SAYTZEFF (*J. Russ. Chem. Soc.*, **24**, 486—491).—Iodobehenic acid, prepared by the direct addition of hydrogen iodide to erucic acid, was gradually added to a solution of an equal weight of caustic potash in 2 parts of 95 per cent. alcohol heated on the water-bath. On completion of the reaction, the alcohol was distilled off, and the soap remaining behind decomposed by means of boiling dilute sulphuric acid. The solid acid obtained in this way was purified by repeated recrystallisation from alcohol, and is called by the authors *isoerucic acid*,

$C_{22}H_{42}O_2$. It melts in a capillary tube at $54-56^\circ$, and solidifies in mass at 54° . From alcoholic solution it separates in small, tabular crystals, but solidifies from the fused state in brilliant stellate aggregates, very like brassidic acid. It combines with bromine, giving a dibromide, $C_{22}H_{42}Br_2O_2$, which fuses at $44-46^\circ$, the corresponding compound from brassidic acid melting at $54-55^\circ$. On reduction with fuming hydriodic acid, it yields behenic acid. When oxidised in dilute alkaline solution with potassium permanganate, it gives a dihydroxy-acid, $C_{22}H_{44}O_4$, melting at $86-88^\circ$. The authors consider that erucic acid has the constitution $CH_3 \cdot [CH_2]_{17} \cdot CH:CH \cdot CH_2 \cdot COOH$, and isoerucic acid, $CH_3 \cdot [CH_2]_{17} \cdot CH_2CH:CH \cdot COOH$. J. W.

Transformation of Elaïdic acid into Oleïc and Iso-oleïc acids.

By I. LEBEDEF (J. Russ. Chem. Soc., 24, 492-495).—The iodo-acid formed by the direct addition of hydrogen iodide to elaïdic acid, if treated with alcoholic potash, gives a mixture of oleïc and of iso-oleïc acids, which may be separated by treating the lead salts with ether.

The iso-oleïc acid obtained in this way melts at $43-45^\circ$. On oxidation with potassium permanganate, it gives an acid $C_{18}H_{36}O_4$, melting at $78-80^\circ$. The same acid is obtained by treating the dibromide with moist silver oxide. The author considers that these results confirm the view that oleïc and elaïdic acids are geometrical isomerides. J. W.

Transformation of Brassidic acid into Erucic and Isoerucic acids.

By N. SAYTZEFF (J. Russ. Chem. Soc., 24, 496-499).—By the addition of hydrogen iodide, brassidic acid may be converted into an iodobehenic acid which, when treated with alcoholic potash, yields the potassium salts of erucic and isoerucic acids. The former is only present in small quantity, isoerucic acid being the chief product of the reaction. The iodobehenic acid prepared from erucic acid yields exactly the same products. J. W.

Oxidation of Brassidic acid. By M. JUKOVSKY (J. Russ. Chem. Soc., 24, 499-501).—When brassidic acid is treated with an equal quantity of potassium permanganate and 30 per cent. of caustic potash in 1.5 per cent. aqueous solution, the reaction proceeds very slowly, and the permanganate is not decolorised until the solution has been heated for a considerable time on the water-bath. Little or no dihydroxybehenic acid is formed under these conditions. If more caustic potash is employed, the yield of dihydroxy-acid is greater, being 10 per cent. of the brassidic acid when 50 per cent. of potash is used, and 20 per cent. with 75 per cent. of potash. The dihydroxybehenic acid obtained in this way differs from the isomeride formed by the oxidation of erucic and isoerucic acids. It is insoluble in water, and dissolves more readily in alcohol than in ether. From ethereal solution, it crystallises in microscopic plates, which melt in a capillary tube at $99-100^\circ$, solidifying again at 88° . The silver salt is a white, insoluble precipitate. J. W.

for 3—4 hours. The pelargonic acid, which is insoluble in water, is best purified by steam distillation. It yields a *barium* salt, which crystallises in lustrous leaflets.

Amidotriskaidecanic hydrochloride, $\text{HCl} \cdot \text{NH}_2 \cdot [\text{CH}_2]_{12} \text{COOH}$, melts at 132° , and is soluble in water. The *free acid* is a white, crystalline powder, and melts at 163° . The *barium*, *calcium*, and *silver* salts are sparingly soluble. The *ethyl* salt melts at 73° , and is strongly alkaline. The *hydrochloride* of the *ethyl* salt crystallises in beautiful, white needles, and melts at 145° .

Oxybrassicidic hydrazide, $\text{N}_2 \cdot [\text{C}(\text{C}_8\text{H}_{17}) \cdot [\text{CH}_2]_{12} \cdot \text{COOH}]_2$, is obtained by heating an alcoholic solution of oxybrassicidic acid, hydrazine sulphate, and sodium hydroxide on the water bath for two hours. It melts at 56° .
E. C. R.

Some Derivatives of Pyruvic acid. By L. SIMON (*Bull. Soc. Chim.* [3], 9, 111—112).—Pyruvic acid, hitherto known only as a liquid, has been obtained as a nearly colourless solid, melting at 9° ; its index of refraction agrees with the theoretical for $\text{CMeO} \cdot \text{COOH}$. The following heats of solution, &c., were observed:— $\text{C}_3\text{H}_4\text{O}_4 + \text{Aq} = 4.4$, $+ \text{NaOHAq} = 11.0$, $+ \text{KOH} = 10.9$, $+ \frac{1}{2}\text{Ba}(\text{OH})_2 = 12.5$ Cal. When oxidised by very dilute alkaline permanganate, it yields acetic acid only. With aniline, ethyl pyruvate gives two yellow, crystalline substances, melting at 144° and 250° , neither of which, consequently, is pyruvic anilide (m. p. 104°).
C. F. B.

Ethylic Pyruvate, and the Product of its Condensation by Hydrogen Chloride. By P. GENYRESSE (*Bull. Soc. Chim.* [3], 9, 377—380).—Pure ethylic pyruvate was prepared by saturating pyruvic acid in twice its weight of absolute alcohol with dry hydrogen chloride at the temperature of a freezing mixture, and fractionating after 24 hours; it boils without appreciable decomposition at 144° ; when treated in ethereal solution with dry ammonia at 18° , it yields a crystalline product, which is unstable, and dissolves freely in water, but only sparingly in ether or alcohol.

The *ethylic salt*, $\text{COOEt} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO} \cdot \text{COOEt}$, is prepared by saturating ethylic pyruvate with hydrogen chloride at the temperature of a mixture of ice and salt, and distilling in a vacuum after 50 days. It is a pale rose-coloured liquid boiling at 170 — 172° at 20 mm. pressure, without decomposition, and at about 225° at the ordinary pressure, with slight decomposition; it dissolves in alcohol, but not in water, by which it is not decomposed even at the boiling point; its specific gravity is 1.161. The corresponding *acid*, $\text{COOH} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO} \cdot \text{COOH}$, could only be obtained as a syrup. The *normal silver salt* is thrown down as a white precipitate on the addition of silver nitrate to a neutralised solution of the acid; the *normal copper salt*, with $2.5\text{H}_2\text{O}$, is a bluish-green powder which is slowly deposited from a mixture of a solution of the neutralised acid with cupric acetate.
A. G. B.

Some new Complex Oxalates. By F. KEHRMANN and N. PICKERSGILL (*Zeit. anorg. Chem.*, 4, 133—137).—Oxalates containing

three metals have been prepared, in the first instance by the action of sodium (or barium or strontium) chloride on double oxalates of potassium with other metals, and subsequently often by crystallising a mixture of the three simple oxalates in the required proportions. They all crystallise in the regular system, some as octahedra with rhombic dodecahedron faces also present, others as triakis tetrahedra, the hemihedral form of the ikositetrahedron. The following have been prepared and analysed: $\text{K}_2\text{NaFe}(\text{C}_2\text{O}_4)_3$, green octahedra; $\text{KNa}_2\text{Al}(\text{C}_2\text{O}_4)_2 + 4\text{H}_2\text{O}$, triakis tetrahedra; $\text{KNa}_2\text{Cr}(\text{C}_2\text{O}_4)_3 + 4\text{H}_2\text{O}$, dark-coloured triakis tetrahedra; $\text{KNa}_2\text{Co}(\text{C}_2\text{O}_4)_3 + 4\text{H}_2\text{O}$, dark-green triakis tetrahedra.

Potassium cobalt oxalate and barium chloride give *barium cobalt oxalate*, $\text{Ba}_3\text{Co}_2(\text{C}_2\text{O}_4)_6 + 12\text{H}_2\text{O}$, as tiny, green needles. *Potassium aluminium oxalate*, $\text{K}_3\text{Al}(\text{C}_2\text{O}_4)_3 + 3\text{H}_2\text{O}$, forms colourless monosymmetric prisms. C. F. B.

Dimolecular Propionic Cyanide. Ethyltartronic acid. By K. BRUNNER (*Monatsh.*, **14**, 120—130).—*Dimolecular propionic cyanide*, $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$ (compare Claisen and Moritz, *Abstr.*, 1881, 154), has been obtained crystallised in the following manner:—Propionic anhydride (20 grams) is dissolved in dry ether (100 c.c.) and powdered potassium cyanide (10 grams) added to the cooled mixture, which is then shaken for three days. More ether (50 c.c.) is added, the mixture cooled and saturated with gaseous hydrogen chloride, and the ethereal layer then poured off through a filter and allowed to evaporate. The crystals which separate are recrystallised from ether, dried on a porous plate, and recrystallised from alcohol; they are then colourless. The substance has an odour of leeks, melts at 58° , and boils at $227\text{--}228^\circ$ (uncorr.) under 740 mm. pressure. With potash, it yields ammonia, hydrogen cyanide, and propionic acid; with phenylhydrazine, propionylphenylhydrazine, $\text{N}_2\text{H}_2\text{Ph}\cdot\text{CEtO}$; with hydrochloric acid, ethyltartronic acid (in addition to propionic acid and ammonia?). This acid, $\text{C}_5\text{H}_8\text{O}_5 + \text{H}_2\text{O}$ (compare Guthzeit, *Abstr.*, 1882, 39), crystallises in tables consisting of two interpenetrating triclinic twins, melts at $64\text{--}70^\circ$, and when anhydrous at $115\text{--}116^\circ$ with decomposition; the *barium salt*, $\text{C}_5\text{H}_6\text{O}_5\text{Ba} + 2\text{H}_2\text{O}$ (the last $\frac{1}{2}\text{H}_2\text{O}$ is lost only at 180°), and the *silver salt*, $\text{C}_5\text{H}_6\text{O}_5\text{Ag}_2$, were prepared and analysed. When distilled, the acid loses carbonic anhydride and forms α -hydroxybutyric acid. Its formation from dipropionic dicyanide is analogous to that of isomalic acid from diacetyl dicyanide. C. F. B.

The Formula of ordinary Tartaric acid. By A. COLSON (*Bull. Soc. Chim.* [3], **9**, 87—90).—A reply to Friedel (this vol., i, 195) and Le Bel, containing also an allusion to Guye's conception of the "product of asymmetry." C. F. B.

Action of Thionyl Chloride on Acid Amides. By A. MICHAELIS and H. SIEBERT (*Annalen*, **274**, 312—315).—The authors find that the acid amides, when treated with thionyl chloride, do not yield thionyl derivatives, in a manner similar to the amines, but that this reagent acts on the amides as a dehydrating agent merely, the corresponding

nitrile being formed together with sulphurous anhydride and hydrogen chloride. The reaction is a general one, and has been applied in the cases of acetamide, propionamide, benzamide, and metanitrobenzamide; it is of importance as a means of preparing the nitriles inasmuch as none but gaseous bye-products are formed.

Metamidobenzamide reacts with thionyl chloride forming a colouring matter which appears to be related to those obtained by warming aromatic primary amines with thionyl chloride. A. R. L.

Dipropylamidoacetic acid. By F. CHANCEL (*Bull. Soc. Chim.* [3], 9, 234—236).—When dipropylamine (3 mols.) is dissolved in alcohol and heated in a sealed tube at 100—110° for 12 hours with bromoacetic acid (1 mol.), *dipropylamidoacetic acid*, $\text{CH}_2\text{NPr}_2\cdot\text{COOH}$, is obtained; the *aurochloride* melts at 127°, and the copper salt crystallises with 1 mol. H_2O . A. R. L.

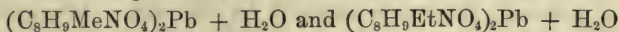
Tripropylamidoacetic acid. By F. CHANCEL (*Bull. Soc. Chim.* [3], 9, 236—238).—When dry tripropylamine and ethylic chloroacetate are heated together on the water-bath, a syrupy mass consisting of ethylic chloroacetate and the *chloride of ethylic tripropylamidoacetate* separates at the end of 30 hours. The latter is dissolved in alcohol and converted into the *platinochloride* by the addition of platinic chloride; this compound on decomposition with hydrogen chloride yields the anhydro-compound $\text{CH}_2\text{<}\begin{smallmatrix} \text{NPr} \\ \text{CO} \end{smallmatrix}\text{>O}$; the *hydrochloride* and other derivatives were prepared. A. R. L.

Oxalyl Derivatives. By T. DECEV (*J. pr. Chem.* [2], 48, 78—80).—*Oxamic acid phenylhydrazine*, $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{N}_2\text{H}_5\text{Ph}$, is obtained by the action of ammonia on ethylic oxalylphenylhydrazine (Abstr., 1887, 138); it crystallises in silky laminae, and melts at 233°. The *methyl derivative*, $\text{NHMe}\cdot\text{CO}\cdot\text{CON}_2\text{H}_5\text{Ph}$, crystallises in silvery prisms, and melts at 186°; the *phenyl derivative* melts at 235°. An *acetyl derivative* melts at 224°.

The *phenylhydrazines of oxaluric and thio-oxaluric acids*, obtained by the action of carbamide and thiocarbamide on ethylic oxalylphenylhydrazine, crystallise in prisms and needles, and melt at 223° and 175° respectively. Ethylic chlorocarbonate forms an oily product with ethylic oxalylphenylhydrazine; this reacts with ammonia to form the *amide*, $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{N}_2\text{HPh}\cdot\text{COOEt}$, which melts at 236°, and the *compound* $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{N}_2\text{HPh}\cdot\text{CO}\cdot\text{NH}_2$, which crystallises in laminae, and melts above 300°. A. G. B.

Action of Ammonia on Mesiten Lactone and its Derivatives. By W. KERP (*Annalen*, 274, 267—284).—Anschütz, Bendix, and Kerp (Abstr., 1891, 173) obtained a compound $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_4$ by passing ammonia into an alcoholic solution of ethylic isodehydracetate; when this is treated with water, it is converted into the so-called basic ammonium salt of ethylic hydroxymesitencarboxylate described by Hantzsch (*Annalen*, 222, 1). The author regards the last-named compound, however, as the hydrate of ethylic ammonium mesiten-

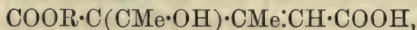
carbamate, $\text{COOEt} \cdot \text{C} \begin{smallmatrix} \text{CMe}:\text{CH} \\ \text{CMe}-\text{O} \end{smallmatrix} > \text{C}(\text{NH}_2) \cdot \text{ONH}_4 + \text{H}_2\text{O}$, and the following experiments lend support to this hypothesis. Analyses of the *lead* salts of both the methylic and ethylic compounds show that they have the compositions



respectively, and are thus derived from the ammonium salts by displacement of NH_4 by Pb. The *cadmium* salt of the methylic compound crystallises with $3\text{H}_2\text{O}$.

Methylic mesitencarbamate, $\text{COOMe} \cdot \text{C} \begin{smallmatrix} \text{CMe}:\text{CH} \\ \text{CMe}-\text{O} \end{smallmatrix} > \text{C}(\text{NH}_2) \cdot \text{OH}$, is obtained by suspending the lead salt in ether and passing in a current of hydrogen sulphide; it crystallises in small, transparent needles, commences to evolve ammonia at 80° , and melts at 92° with decomposition, yielding methylic isodehydracetate. *Ethylic mesitencarbamate* melts at 82° with decomposition. Whereas aqueous hydrochloric acid converts alkylic mesitencarbamates into the corresponding alkylic isodehydracetates, alcoholic hydrogen chloride converts them into the lactams (alkylic oxylutidinecarboxylates).

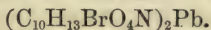
When treated with hydrochloric acid, the alkylic ammonium mesitencarbamates yield hydroxymesitencarboxylates,



and are regenerated when the latter are treated with ammonia.

When bromomesitenlactone (m. p. $106-107^\circ$) is heated at 100° with aqueous ammonia, *bromo-ψ-lutidostyryl*, $\text{C}_7\text{H}_5\text{BrNO}$, is obtained; this melts at $186-187^\circ$, dissolves sparingly in water, the solution having a faint alkaline reaction, and, on bromination, yields a *dibromo*-derivative melting at 235° with decomposition.

The *lactam* (ethylic bromhydroxylutidinecarboxylate), $\text{C}_{10}\text{H}_{12}\text{BrNO}_3$, is obtained by passing dry ammonia into ethylic isodehydracetate at 100° , or by brominating ethylic hydroxylutidinecarboxylate; it melts at 157° . When carefully dried ammonia is passed into an alcoholic ethereal solution of ethylic bromisodehydracetate, the compound $\text{COOEt} \cdot \text{C} \begin{smallmatrix} \text{CMe}:\text{CBr} \\ \text{CMe}-\text{O} \end{smallmatrix} > \text{C}(\text{NH}_2) \cdot \text{ONH}_4$ is formed; it is much more stable than the non-brominated compound (see above), melts at 122° with decomposition, and forms an *anhydrous lead salt*,



Other instances are on record of the formation of salts by the addition of a base to a lactone; thus Perkin (this Journal, 1868, 191) and Williamson (*ibid.*, 1875, 850) show that coumarin forms additive compounds with alkalis capable of being reconverted into coumarin by acids.

A. R. L.

Adipin Ketone. By W. HENTZSCHEL and J. WISLICENUS (*Annalen*, 275, 312-317).—When anhydrous calcium adipate is distilled, *adipin ketone*, $\text{CO} < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$, passes over between 128° and 130° ; it may be purified by conversion into its compound with hydrogen sodium

sulphite; it is a mobile liquid, having the odour of peppermint; it boils at $130\text{--}130.5^\circ$ (corr.), has a sp. gr. at $21.5/4^\circ = 0.9416$, and is sparingly soluble in water. From the higher boiling portion of the above crude distillate, a compound, $C_{10}H_{14}O$, can be isolated; this is a bluish oil, which boils at $139\text{--}141^\circ$ (30 mm.) and becomes brownish-yellow if allowed to remain exposed to the air. *Adipinketoxime*, $C_8H_8\cdot NOH$, forms long, glittering, friable prisms, melts at 56.5° , boils at $120\text{--}121^\circ$ under a pressure of 45 mm., and at $196\text{--}196.5^\circ$ under 756 mm. pressure; it is decomposed into the ketone when warmed with dilute sulphuric acid.

When adipin ketone is gradually added to warmed nitric acid of sp. gr. 1.2, it yields glutaric acid and a little succinic acid.

A. R. L.

Adipin Ketone from Wood Oil. By W. HENTZSCHEL (*Annalen*, **275**, 318—322).—A ketone-like compound was isolated by Claisen (*Ber.*, **8**, 1258) and by Pinner (*Ber.*, **15**, 594) from the higher boiling fraction obtained in the rectification of wood spirit. Some of this substance boiling between 120° and 140° was shaken with sodium hydrogen sulphite, and the crystalline compound decomposed with soda, when adipin ketone (see preceding abstract) was obtained.

A. R. L.

Pentamethylenic Alcohol and its Derivatives. By J. WISLICENUS and W. HENTZSCHEL (*Annalen*, **275**, 322—330).—When adipin ketone is mixed with its own volume of ether, poured into an equal volume of water, and treated with sodium in a reflux apparatus,

pentamethylenic alcohol, $\begin{array}{c} CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2 \end{array} > CH\cdot OH$, is obtained. It is a colour-

less oil, very slightly soluble in water, and has the odour of amylic alcohol; its sp. gr. at $21.5/4^\circ$ is 0.9395, and it boils at 139° ; on oxidation with dilute nitric acid, it yields glutaric and succinic acids. The *iodide*, C_5H_9I , boils at $166\text{--}167^\circ$ (corr.) under a pressure of 754 mm., and has a sp. gr. at $22/4^\circ = 1.6945$. The *bromide*, C_5H_9Br , boils at $136\text{--}138^\circ$, and has a sp. gr. at $22(?)/4^\circ = 1.3720$. The *amine*, $C_5H_9\cdot NH_2$, obtained by reducing the ketoxime (preceding abstract) with sodium and alcohol, is a colourless liquid having a fishy, ammoniacal odour; it boils at $106\text{--}108^\circ$, fumes in contact with carbonic anhydride, and combines with water with development of heat. The *hydrochloride* crystallises in needles, and is very hygroscopic; the *sulphate* forms silky plates.

Pentamethylene, $CH_2 < \begin{array}{c} CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2 \end{array}$, is obtained by reducing an alcoholic solution of pentamethylenic iodide with zinc and hydrochloric acid. It boils at $50.25\text{--}50.75^\circ$, has a sp. gr. at $20.5/4^\circ = 0.7506$, and a refractive index at $20.5^\circ = 1.4039$, whence its molecular refraction $m \frac{n-1}{d} = 37.667$ or $M \frac{n^2-1}{(n^2+2)d} = 22.799$, which fully establishes its

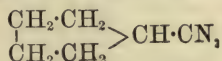
cycloïd nature. It behaves as a saturated compound towards bromine, and the halogen is absorbed with the evolution of hydrogen bromide in direct sunlight. Bromine acts slowly on it in the dark at 100° ; but at $128\text{--}130^\circ$, when separation of carbon takes place, the

product consists of unaltered hydrocarbon and pentamethylenic bromide.
A. R. L.

Pentamethenylene and its Dibromide. By C. GÄRTNER (*Annalen*, 275, 331—332).—Pentamethenylene, $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2\text{CH} \\ | \\ \text{CH}_2\text{CH} \end{smallmatrix}$, is obtained by warming iodopentamethylene (preceding abstract) with alcoholic potash. Almost the whole of the product passes over at 45° . It forms a *dibromide*, $\text{C}_5\text{H}_8\text{Br}_2$, which is a yellowish oil boiling at $105\text{--}105.5^\circ$ (45 mm.).
A. R. L.

Pentamethylenecarboxylic acid. By C. GÄRTNER (*Annalen*, 275, 333—341).—When adipin ketone (this vol., i, 555) is dissolved in ether, poured upon pulverised potassium cyanide, and concentrated hydrochloric acid added, with cooling, *α -hydroxypentamethylenecarboxylic acid*, $\begin{smallmatrix} \text{CH}_2\text{CH}_2 \\ | \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} > \text{C}(\text{OH})\cdot\text{COOH}$, is obtained. It crystallises from water in small, colourless needles, and melts at 103° . The *calcium* salt crystallises with $6\text{H}_2\text{O}$, the *silver* salt is anhydrous, and the *zinc* salt crystallises with $2\text{H}_2\text{O}$.

When iodopentamethylene is dissolved in 80 per cent. alcohol (3 parts) and heated at 200° in a sealed tube with a slight excess of pulverised potassium cyanide, *pentamethylenic nitrile*,



boiling at $170\text{--}171^\circ$, is the chief product. It is converted into the corresponding *carboxylic acid*, $\text{C}_6\text{H}_9\text{COOH}$, when heated on the water-bath with concentrated hydrochloric acid for eight hours; the yield is small. The acid has an unpleasant odour; it boils at $214\text{--}215^\circ$, solidifies at -7° , and melts at between -4° and -3° . It is also formed by heating *α -hydroxypentamethylenecarboxylic acid* with hydriodic acid and phosphorus at $190\text{--}195^\circ$ in a sealed tube for five hours. The *calcium* salt crystallises with $5\text{H}_2\text{O}$, the *barium* salt with $1\text{H}_2\text{O}$, and the *silver* salt is anhydrous and fairly stable towards light. When *α -hydroxypentamethylenecarboxylic acid* is heated on the water-bath with hydriodic acid and phosphorus, a small quantity of an *acid*, $\text{C}_6\text{H}_9\text{O}$, is formed, the nature of which has not yet been determined; it melts at 120° .
A. R. L.

Constitution of Suberone and of the Closed-chain Ketones of Pimelic and Azelaic acids. By H. MAGER (*Annalen*, 275, 356—366).—The best yield of suberone is obtained by distilling calcium suberate (15 grams at most). The *α -pimelic acid*, which is obtained by the oxidation of suberone (Schorlemmer and Dale, this Journal, 1874, 934), is shown to be identical with that prepared by W. H. Perkin, jun. (*Ber.*, 18, 3249) from ethylic malonate and trimethylene dibromide; so that there is no doubt that suberone has the formula assigned to it by Schorlemmer and Dale.

When dehydrated calcium pimelate is distilled, a closed-chain

Ketone, $C_6H_{10}O$, is obtained; it is a colourless oil having the odour of peppermint, boils at $152-155^\circ$, and yields adipic acid on oxidation with nitric acid.

Schorlemmer and Dale (*loc. cit.*) obtained normal heptane, together with an oil having the odour of suberone, by the distillation of anhydrous calcium azelate. The author has repeated this experiment, and obtained normal heptane, together with a *ketone*, $C_8H_{14}O$, having a peppermint-like odour, and boiling at $90-91^\circ$ (23 mm.); on oxidation with potassium permanganate, it gives a bibasic hydroxy-acid, $C_8H_{14}O_5$, melting at about 100° . A. R. L.

Constituents of Wood Oil. By E. LOOFT (*Annalen*, 275, 366—382).—A quantity of wood oil was fractionally distilled, and the two principal fractions boiling at $120-140^\circ$ and $160-180^\circ$ examined as follows.

The fraction boiling at $120-140^\circ$ was shaken with a concentrated solution of hydrogen sodium sulphite, and, after collecting the crystals of the sulphite compound of adipin ketone, the filtrate was mixed with a fresh quantity of the salt solution, when it separated into an oily and an aqueous layer. The former boiled at $129-132^\circ$, and consisted chiefly of isoamylic alcohol, but after re-fractionation a little pyridine was isolated from the fraction of lower boiling point; the portion boiling at about 140° was soluble in mineral acids, and consisted, therefore, probably of methylpyridines.

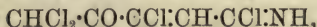
The chief portion of the fraction boiling at $160-180^\circ$ consisted of the *ketone* C_6H_8O , a translucent oil of aromatic odour boiling at 157° ; it had a sp. gr. of 0.98075 at 16° , and a refractive index of 1.4762 at 15° . The *oxime*, C_6H_8NOH , crystallises in nacreous plates, melts at 128° , and forms a dibromo-additive compound melting at 99° . The ketone yields acetic and succinic acids on oxidation with potassium permanganate. The only formula which is in accord with these facts is the following, $CH_2 < \begin{matrix} CH_2 \cdot CO \\ | \\ CH_2 \cdot CMe \end{matrix}$. When the ketone is

shaken with hydrogen sodium sulphite solution, a thick magma of crystals of the *sulphite* compound is formed; dissolution subsequently ensues, however, with rise of temperature, and when the solution is concentrated, sulphurous anhydride is evolved, and, on cooling, large, flat crystals separate out of the composition $C_{12}H_{18}S_2O_8Na_2 + H_2O$. When barium chloride is added to a solution of this salt, the *barium* salt, $C_{12}H_{18}S_2O_8Ba + 3H_2O$, is obtained; the *silver* salt is readily soluble in hot water, and fairly stable towards light. The acid has not yet been prepared, and experiments on its constitution are in progress. A. R. L.

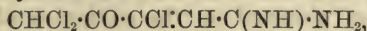
Imido-derivatives of Chlorinated Diketopentene. By T. ZINCKE and O. FUCHS (*Ber.*, 26, 1666—1681).—The chlorinated δ -ketonic acids obtained from the ketochlorides of resorcinol and orcinol when treated with ammonia yield imidoketones with elimination of 1 mol. of carbonic anhydride and 3 mols. of hydrogen chloride (this vol., i, 259). Those compounds are obtained by treating the

finely-divided ketonic acids, either suspended in water or dissolved in sodium acetate, with an excess of dilute ammonia, keeping the mixture well cooled with ice.

Dichlorimidoketopentene, $\begin{array}{c} \text{CH}\cdot\text{C}(\text{NH}) \\ \parallel \\ \text{CCl}-\text{CO} \end{array} > \text{CHCl}$, is obtained from the acid $\text{CHCl}_2\cdot\text{CO}\cdot\text{CCl}\cdot\text{CH}\cdot\text{CCl}_2\cdot\text{COOH}$. It crystallises in long, white, interlacing needles, melts at 174° , sublimes at a lower temperature, and yields an easily soluble sodium salt. The *imidochloride*,



is obtained by treating it in chloroform solution with excess of chlorine. It crystallises in colourless prisms, melts at 130° , is insoluble in water, hydrochloric acid, and soda, and is easily converted into the amide and amidine. The *amide*, $\text{CHCl}_2\cdot\text{CO}\cdot\text{CCl}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2$, is obtained by treating the imidochloride with sodium hydroxide, adding hydrochloric acid, and extracting with ether. It may also be obtained by saturating with chlorine the acetic acid solution of the imidoketone. It crystallises in beautiful, colourless prisms or radiating needles, melts at $167-168^\circ$, dissolves in cold sodium hydroxide without decomposition, and is converted into the corresponding acid when heated with hydrochloric acid at 100° . The *amidine*,

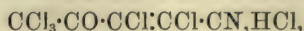


is obtained by dissolving the imidochloride in alcoholic ammonia, and evaporating to dryness on the water-bath. It crystallises in colourless, radiating needles, melts at $143-144^\circ$, and has basic properties.

Trichlorimidoketopentene, $\begin{array}{c} \text{CH}\cdot\text{C}(\text{NH}) \\ \parallel \\ \text{CCl}-\text{CO} \end{array} > \text{CCl}_2$, obtained from the acid $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}\cdot\text{CH}\cdot\text{CCl}_2\cdot\text{COOH}$, crystallises in long, white needles, melts at 207° , and yields an easily soluble sodium salt which crystallises in long, slender needles. An acetyl derivative could not be obtained. Methyl iodide is without action on the compound. When treated with sodium hydroxide, it is decomposed with evolution of ammonia; ammonia is also formed when it is treated with sodium amalgam. The *imidochloride*, $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}\cdot\text{CH}\cdot\text{CCl}\cdot\text{NH}$, is obtained by treating it, dissolved in acetic acid, with excess of chlorine. It crystallises in beautiful, nacreous leaflets or tablets, melts at $141-142^\circ$, and is decomposed when heated with water. The *amide*, $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in short spears or large, colourless prisms, melts at $107-108^\circ$, and is soluble in hot water and dilute hydrochloric acid. When heated with concentrated hydrochloric acid in a sealed tube at 100° , it is converted into trichloroacetyl- β -chloroacrylic acid, $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}\cdot\text{CH}\cdot\text{COOH}$, which melts at 126° (this vol., p. 317).

Tetrachlorimidoketopentene, $\begin{array}{c} \text{CCl}\cdot\text{C}(\text{NH}) \\ \parallel \\ \text{CCl}-\text{CO} \end{array} > \text{CCl}_2$, is obtained from the acid $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}\cdot\text{CCl}\cdot\text{CCl}_2\cdot\text{COOH}$. The yield is not good, as a second reaction takes place with evolution of chloroform, and formation of a compound having the composition $\text{C}_5\text{Cl}_4\text{O}_2\text{NH}$, and melting at 80° . The tetrachlorimidoketone is also obtained by heating the amide $\text{CHCl}_2\cdot\text{CO}\cdot\text{CCl}\cdot\text{CCl}\cdot\text{CONH}_2$ with concen-

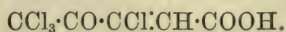
trated sulphuric acid. It crystallises in long, colourless, felted needles, melts at 203° , and gives a sodium salt which crystallises in beautiful, iridescent leaflets, effloresces on exposure to air, and is decomposed by boiling with water or alcohol. When reduced with hydrogen iodide or sodium amalgam, ammonia is formed. When reduced with sodium in alcoholic solution, a base is obtained which is probably amidopentamethylene. The *imidochloride*,



crystallises in radiating prisms, and melts at 111° . The amide has already been described (Abstr., 1892, 1186). It melts at $145\text{--}146^{\circ}$. The acid obtained from it by heating with hydrochloric acid melts at $85\text{--}86^{\circ}$ when dry, and at $51\text{--}52^{\circ}$ when hydrated.

Trichlorimidoketomethylpentene, $\begin{array}{c} \text{CMe}\cdot\text{C}(\text{NH}) \\ \parallel \\ \text{CCl} \text{---} \text{CO} \end{array} > \text{CCl}_2$, has already been described (this vol., i, 259). It melts at $187\cdot5^{\circ}$. The *imidochloride*, $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}\cdot\text{CMe}\cdot\text{CCl}\cdot\text{NH}$, crystallises in beautiful, colourless prisms, and melts at 110° . The *amide*, $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}\cdot\text{CMe}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in white, radiating needles or long leaflets, melts at $117\text{--}118^{\circ}$, and when heated with concentrated hydrochloric acid at 150° is converted into the acid $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}\cdot\text{CMe}\cdot\text{COOH}$, which is identical with that obtained by the oxidation of the ketonic acid from pentachlororcinol.

Dichloracetyl- β -chloracrylic acid, $\text{CHCl}_2\cdot\text{CO}\cdot\text{CCl}\cdot\text{CH}\cdot\text{COOH}$, is obtained from the above trichlorimidoketopentene by heating it with concentrated hydrochloric acid at 100° . It crystallises in concentric prisms or tablets, melts at $106\text{--}107^{\circ}$, and, when treated with hypochlorous acid, is easily converted into the acid



Dichloracetyldichloracrylic acid, $\text{CHCl}_2\cdot\text{CO}\cdot\text{CCl}\cdot\text{CCl}\cdot\text{COOH}$, is obtained from tetrachlorimidoketopentene by heating it with hydrochloric acid at 150° , but can be more easily prepared by heating the amide $\text{C}_5\text{Cl}_4\text{H}_3\text{NO}_2$ (Abstr., 1891, 689) with concentrated hydrochloric acid. It crystallises in colourless prisms, and melts at 71° .

Dichloracetylchloromethylacrylic acid, $\text{CHCl}_2\cdot\text{CO}\cdot\text{CCl}\cdot\text{CMe}\cdot\text{COOH}$, crystallises in short, colourless needles and prisms, and melts at $105\text{--}106^{\circ}$. When treated with dilute bleaching powder solution, it yields the acid $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}\cdot\text{CMe}\cdot\text{COOH}$ (this vol., i, 317).

E. C. R.

Action of Nascent Bromine on some Benzene Derivatives.

—By W. VAUBEL (*J. pr. Chem.* [2], 48, 75—78).—This investigation was conducted by adding sulphuric acid and potassium bromide to an aqueous solution (where possible) of the benzene derivative to be investigated, and pouring into the mixture an aqueous solution of the calculated quantity of potassium bromate. The following general results were noted: the groups OH and NH_2 favour the entry of bromine into the ortho- and para-positions; two of these groups in the meta-position to each other will both influence the bromine substitution in this sense, but they militate against it when they are in

the ortho- and para-positions relatively to each other. These observations confirm the author's previously expressed opinions with regard to the configuration of benzene (Abstr., 1891, 1343). A. G. B.

Iodoso- and Iodoxy-compounds. By C. WILLGERODT (*Ber.*, 26, 1802—1811).—The first portion of this paper consists of a reply to the criticisms of Askenasy and Mayer (this vol., i, 503), in which the author maintains the correctness of the results he has already published. The second portion gives a further account of the meta-nitroiodoso- and nitroiodoxy-compounds (compare this vol., i, 256).

The metanitroiodosobenzene already described commences to decompose at a low temperature, and it is the first products of decomposition which are completely split up at 195°. Paranitroiodosobenzene explodes without report at 82—83°, the products formed being paranitriodobenzene and iodic anhydride. It is also converted by acetic acid into the *acetyl* derivative, which separates as a pale yellow substance if only a small quantity of acetic acid is employed. On boiling with water, it is converted into paranitriodobenzene and *paranitriodoxybenzene*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{IO}_2$, the yield of the latter being small. It crystallises from acetic acid in colourless, transparent, six-sided plates, and explodes at 212—213°.

Orthonitriodobenzene combines with chlorine in chloroform solution yielding *orthonitrophenyl iodochloride*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{ICl}_2$, which is a yellow, crystalline mass, and melts at 96° with violent decomposition. It cannot be recrystallised without undergoing change, and is readily converted into *orthonitroiodosobenzene*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{IO}$, in the usual manner; the latter crystallises in orange-yellow prisms, and decomposes at about 100°, the product being impure orthonitriodoxybenzene. With acetic acid, it yields an acetate which separates in compact crystals, decomposes at 145° with much frothing, and on exposure to the air again forms orthonitroiodosobenzene. *Orthonitriodoxybenzene*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{IO}_2$, obtained from the iodoso-derivative in the usual manner, crystallises from acetic acid in thin, transparent, yellowish tablets, and explodes with a sharp report at about 210°.

H. G. C.

Action of Aluminium Chloride on Chlorides and Bromides of Aromatic Radicles. By J. SCHRAMM (*Ber.*, 26, 1706—1709).—Benzyl chloride yields with aluminium chloride, alone or in carbon bisulphide solution, a substance which, when distilled, decomposes into toluene and anthracene; if benzene is used as a solvent, anthracene and diphenylmethane are formed. α -Chlorethylbenzene, CPhMeHCl , with aluminium chloride in benzene solution at 0°, yields unsymmetrical diphenylethane, ethylbenzene, and symmetrical mesodimethyldihydroanthracene, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CHMe} \\ \text{CHMe} \end{smallmatrix} > \text{C}_6\text{H}_4$, the first being doubtless formed by the combination of benzene with cinnamene, itself obtained from the chlorethylbenzene by loss of hydrogen chloride. The product obtained by chlorinating boiling ethylbenzene (? ω -chlorethylbenzene, $\text{CH}_2\text{Ph} \cdot \text{CH}_2\text{Cl}$), if mixed with aluminium chloride at 0°, yields dibenzyl, anthracene, and unsymmetrical diphenylethane; the author asserts that the first two are

formed from $\alpha\omega$ -dichlorethylbenzene, the last one from α -chlorethylbenzene, both contained in the crude product of chlorination. $\alpha\omega$ -Dibromomethylbenzene yields dibenzyl, anthracene, and bromobenzene; the formation of the last compound shows that some of the original substance must have decomposed into bromine and cinnamene.

C. F. B.

Some Substituted Benzenoid Hydrocarbons. By P. GEN-VRESSE (*Bull. Soc. Chim.* [3], 9, 219—227).—The heat of combustion of propylbenzene is at constant volume +1246.9 Cal., at constant pressure +1248.6 Cal. Hence the heat of formation C_9 (diamond) + O_2 (gas) = C_9H_{12} (liquid) +14.1 Cal. Errera, by chlorinating the boiling hydrocarbon, obtained a chloropropylbenzene, which gave allylbenzene when treated with alcoholic potash. The author has subjected the vapour of boiling propylbenzene to the action of a slow current of chlorine in a reflux apparatus, until a thermometer plunged into the vapour indicated a temperature of 200°. The product is a chloropropylbenzene, boiling at 208—210° with slight decomposition; it does not attack the eyes, and its sp. gr. is 1.0687. When heated with a concentrated solution of potassium carbonate in a sealed tube at 180—200° for two days, allylbenzene and a *chloropropylbenzene* boiling at 205—206° is obtained. The latter resists the action of potassium carbonate, but is converted into allylbenzene by alcoholic potash, and yields benzoic acid when boiled with alkaline potassium permanganate. Evidence is, therefore, afforded of the existence in the above product of two chloropropylbenzenes containing chlorine in the side chain.

The heat of combustion of isopropylbenzene at constant volume is +1248 Cal., and at constant pressure +1249.9 Cal., so that its formation from its elements develops +17.2 Cal. When isopropylbenzene is chlorinated in the manner described above, it yields *parachlorisopropylbenzene*, boiling at 204—206° with slight decomposition, and at 125° under a pressure of 20 mm. It attacks the eyes, has a sp. gr. = 1.0782, and gives parachlorobenzoic acid on oxidation with alkaline potassium permanganate.

Diisopropylbenzene (b. p. 203—205°) yields terephthalic acid on oxidation with potassium permanganate, and must, therefore, have its two isopropyl groups in the para-position relatively to each other (Beilstein).

The chief product obtained by treating toluene with propylic bromide and aluminium chloride appears from its behaviour on oxidation to be a mixture of 1 : 3-methylpropylbenzene (1 part) and 1 : 4-methylpropylbenzene (5 parts); but it also contains a smaller quantity of isopropyltoluene (see below). It boils at 178—180°; its heat of combustion at constant volume is 1404.2 cal., and at constant pressure 1406.1 Cal., from which the heat of formation +17.9 Cal. is deduced. A *chloro*-derivative boiling at 218—220° was obtained, which, on heating with potassium carbonate, yielded allyltoluene; a small quantity of substance (probably an isomeride) remains unattacked by the potassium carbonate.

The isopropyltoluene mentioned above is a mixture of the 1 : 4-com-

pound, cymene (5 parts), and the 1:3-compound (1 part); it boils at 173° . The heat of combustion at constant volume is $+1407\cdot25$ Cal., and at constant pressure $+1410\cdot1$ Cal., whence its heat of formation is $+9\cdot9$. A. R. L.

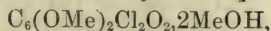
Cinnamene Hydrochloride and Hydrobromide. By J. SCHRAMM (*Ber.*, 26, 1709—1711).—Reasoning from analogy, one would expect the additive compounds of cinnamene with hydrochloric and hydrobromic acids to have the constitution CPhMeHX . Bernthsen and Bender, however (*Abstr.*, 1883, 70), attribute to the hydrobromide the constitution $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Br}$. The author has reinvestigated the matter, and finds that both the hydrochloride and hydrobromide react as if they possessed the first mentioned formula; when boiled in alcoholic solution with potassium cyanide, and then with potash, they yield the ether $\text{CPhMeH}\cdot\text{OEt}$ and no hydrocinnamic acid; with sodium they yield dimethyldiphenylethane, and the hydrochloride with aluminium chloride in benzene solution yields unsymmetrical diphenylethane and mesodimethyldihydranthracene (compare preceding abstract). C. F. B.

Homologues of Phenol. By B. FISCHER and B. GRÜTZNER (*Ber.*, 26, 1646—1649).—*Tertiary amylphenol*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_2\text{Et}$, is obtained by heating phenol with dimethylethylcarbinol and zinc chloride in a reflux apparatus at 180° . It crystallises from light petroleum in long, interlacing needles, melts at $93\text{--}94^{\circ}$, boils at $265\text{--}267^{\circ}$, is volatile with steam, and has a pleasant aromatic odour resembling that of thymol. The *sodium* salt crystallises in white scales, and absorbs carbonic acid from the air. The *acetyl derivative* is a colourless oil, which boils at $264\text{--}266^{\circ}$, and is easily decomposed by sodium hydroxide.

Amylanisole, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}_5\text{H}_{11}$, obtained by heating amylphenol with potassium hydroxide and methylic iodide, is an oil, and boils at $240\text{--}241^{\circ}$. E. C. R.

Supposed Formation of Orthocresol from Methylsalicylic acid [$\text{COOH} : \text{OH} : \text{Me} = 1 : 2 : 5$]. By P. DE CHAMBRIER (*Ber.*, 26, 1692—1694).—Methylsalicylic acid [$\text{COOH} : \text{OH} : \text{Me} = 1 : 2 : 5$], on distillation with lime, yields paracresol, not orthocresol, as stated by O. Jacobson (*Ber.*, 11, 377), together with a little phenol, the formation of the latter being probably due to oxidation by the lime of a part of the methylsalicylic acid to hydroxyisophthalic acid. Reuter's assertion that dimethylsalicylic acid [$\text{COOH} : \text{OH} : \text{Me} : \text{Me} = 1 : 2 : 4 : 5$], on distillation with lime, yields metaxylenol [$\text{Me} : \text{Me} : \text{OH} = 1 : 3 : 4$] (*Ber.*, 11, 30) is also unlikely to be correct. J. B. T.

Hemiacetals derived from Substituted Chloranils. By C. L. JACKSON and H. S. GRINDLEY (*Ber.*, 26, 1631—1633; see also this vol., ii, 322).—When diphenoxydichloroquinone is treated with sodium methoxide, a derivative of dimethoxydichloroquinone,



is obtained. It is a white substance, and when heated at $170\text{--}173^{\circ}$,

is converted into the dimethoxydichloroquinone melting at 141—142°. The same change takes place when the compound is treated with sulphuric or hydrochloric acid, or is boiled with water or dilute alcohol, or when the sodium salt is heated with benzoic chloride or acetic anhydride.

Sodium ethoxide reacts in the same way, and yields a compound of the formula $C_6(OEt)_2Cl_2O_2 \cdot 2EtOH$, which, when heated at 140—143°, is converted into diethoxydichloroquinone melting at 104—105°.

The authors are studying the action of sodium alkyl oxides on various quinones.

E. C. R.

Action of Acid Chlorides on Nitrosodimethylaniline. By P. EHRLICH and G. COHN (*Ber.*, 26, 1756—1757).—The authors have found that acid chlorides combine very readily with nitrosodimethylaniline and other nitroso-derivatives, forming additive compounds, the reaction being sufficiently violent to render dilution with benzene advisable.

With benzoic chloride and nitrosodimethylaniline, an almost quantitative yield of the new compound is obtained; it forms a yellowish precipitate, and if quickly dried may be kept for some time. It is precipitated from alcoholic solution on the addition of ether in white, unstable plates, which have the composition $C_{15}H_{15}N_2O_2Cl$, and the substance is therefore formed by the direct union of the two components. Two formulæ are possible for such a product, namely, $NMe_2 \cdot C_6H_4 \cdot NCl \cdot OBz$ and $NMe_2Cl \cdot C_6H_4 \cdot N \cdot OBz$, of which the authors regard the latter as the more probable. The most remarkable property of the new compound is the readiness with which it reacts with bases and phenols, to form colouring matters, even in the cold. When alcoholic solutions of the new compound and of toluylenediamine are mixed, an intense blue coloration is immediately produced, which does not deepen on keeping.

H. G. C.

Products of the Action of Aniline on Dibromosuccinic acid. By A. REISSERT (*Ber.*, 26, 1758—1765).—Some years ago the products of the action of aniline on dibromosuccinic acid were examined by the author and Tiemann, who obtained a mixture of two acids having the composition $C_{16}H_{14}N_2O_3$ and $C_{16}H_{12}N_2O_2$, and containing therefore respectively the elements of 1 and 2 mols. of water less than the expected dianilidosuccinic acid. The same compounds were also obtained shortly afterwards by Michael, who regarded them as anilidomaleïnanilic acid and anilidomaleïnanil (*Abstr.*, 1886, 698). As the latter compound has recently been obtained by Bischoff (this vol., i, 55) by the action of phosphorus pentachloride on the dianilide of tartaric acid, it can hardly have the constitution assigned to it by Michael; the author has therefore reinvestigated the subject with the following results.

The substance obtained by boiling dibromosuccinic acid (1 mol.) with 10 times its weight of aniline (6 mols.) consists of the compound $C_{16}H_{12}N_2O_2$, and of the aniline salt of the acid $C_{16}H_{14}N_2O_3$, together with a small quantity of the aniline salt of β -anilidoacrylic acid. If the mixture is boiled with aqueous soda, aniline is liberated, and on

the addition of acetic acid, β -anilidoacrylic acid separates, mixed with some dianilidosuccinic acid, whilst the addition of hydrochloric acid causes a fresh precipitate, consisting chiefly of the dianilido-acid.

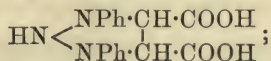
β -Anilidoacrylic acid, $\text{NPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{COOH}$, is best obtained pure by recrystallising its sodium salt from 80 per cent. alcohol, acidifying, and extracting with ether. It is a very unstable substance, and cannot be recrystallised; it becomes coloured at 100° , sinters at 150° , and melts with decomposition at 160° . The sodium salt crystallises in small, lustrous, indistinct crystals.

Dianilidosuccinic acid may be obtained from the impure product described above by recrystallising the sodium salt from absolute alcohol, and saturating the aqueous solution with hydrogen chloride. The properties observed agree with those described by Gorodetski and Hell (Abstr., 1888, 951).

As already stated, Michael regarded the acid $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_3$ as anilido-maleinanilic acid, $\text{COOH}\cdot\text{C}(\text{NPh})\cdot\text{C}\cdot\text{CO}\cdot\text{NPh}$, but in view of Bischoff's synthesis, this view is no longer tenable, and the author believes that it is an anhydro-compound, having probably the con-

stitution
$$\begin{array}{c} \text{NPh}\cdot\text{CH}\cdot\text{COOH} \\ | \\ \text{CO}-\text{CH}\cdot\text{NPh} \end{array}$$
 The second compound, $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2$, which Michael believed to be anilidomaleinanil, is being further investigated by Bischoff, and has therefore not been examined by the author, who, however, proposes to term it for the present *dianilsuccin*.

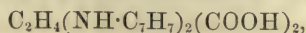
Dinitrosoanilidosuccinic acid, $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4(\text{NO})_2$, is obtained by the careful addition of hydrochloric acid to a solution of sodium nitrite and the sodium salt of the acid, and forms yellow, indistinct crystals; it melts at $142\cdot5^\circ$, and shows Liebermann's reaction. On reduction with zinc and acetic acid, it does not yield the corresponding diphenylhydrazidosuccinic acid, as the latter probably at once loses ammonia, forming *diphenylosotriazolidinedicarboxylic acid*,



this forms a light, white, amorphous mass, which is decomposed by boiling with water, and melts with much frothing at 95° .

H. G. C.

Action of Paratoluidine on Dibromosuccinic acid: New Derivatives of Dianilidosuccinic acid. By A. JUNGAHN and A. REISSERT (*Ber.*, 26, 1766—1773; compare preceding abstract).—Paratoluidine acts on dibromosuccinic acid in a very similar manner to aniline, yielding a mixture of different substances. When the product is treated with alkalis, paratoluidine is liberated, and part of the remainder goes into solution; the residue, after repeated crystallisation from alcohol, forms golden-yellow, lustrous plates, and melts at 228° . It has the composition $\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}_2$, and corresponds exactly with the indifferent compound obtained from aniline, and may therefore be termed *diparatolilsuccin*. The acid corresponding with anhydrodianilidosuccinic acid could not be obtained pure, as it readily takes up water, forming *diparatoluidosuccinic acid*,



which may be prepared from the mixture in a similar manner to the corresponding anilido-derivative. It is a crystalline substance, which becomes yellow at 100° and melts at about 200° ; the *sodium* salt forms stellate groups of hair-like needles, the *calcium* salt a white, flocculent precipitate, the *copper* salt a grass-green precipitate, and the *ethylic* salt white needles, melting at 169° . The *dinitroso*-derivative, $C_{18}H_{18}N_2O_4(NO)_2$, crystallises in small needles, melts at 125° , and gives Liebermann's reaction.

If the sodium salt of the acid is boiled with acetic anhydride, it is converted into a substance which forms small, prismatic crystals, blackens at 215° , and decomposes completely at 222° . It is derived from the *diacetyldiparatoluidosuccinic acid* first produced, by the loss of 2 mols. H_2O , and is converted into the acid by boiling with 10 per cent. alkali, and adding hydrochloric acid; the latter crystallises with $1H_2O$, in small prisms, becomes yellow at 170° , and decomposes completely at 204° . The *calcium* and *barium* salts also contain $1H_2O$. When the acid is boiled with acetic anhydride, it yields the corresponding anhydride, $C_{22}H_{22}N_2O_5$, a white, crystalline substance, which melts at 232° with evolution of gas and previous darkening.

If the sodium salt of dianilidosuccinic acid is boiled with acetic anhydride, it yields the *diacetyldianilidosuccinic* anhydride, but this compound could in no way be made to yield a substance containing 2 mols. less H_2O than the diacetyldianilidosuccinic acid. The *anhydride* $NAcPh \cdot CH \cdot CO$
 $NAcPh \cdot CH \cdot CO > O$ forms white needles, and melts at 192° ; the acid itself crystallises in white prisms containing $1H_2O$, and melts at 172 – 173° . The *silver* salt is a white, flocculent precipitate, and contains no water of crystallisation, whilst the *sodium* and *calcium* salts are crystalline substances, and contain $6H_2O$ and $2H_2O$ respectively.

H. G. C.

Electrolytic Reduction of Aromatic Nitro-compounds. By L. GATTERMANN (*Ber.*, 26, 1844–1856).—The nitro-compound is dissolved in 5 to 10 times its weight of concentrated sulphuric acid, and the cold solution put into a porous cell, which stands in a beaker containing 75–100 per cent. sulphuric acid. The inner cell contains a platinum cathode, and the outer cell a platinum anode. A current of $1\frac{1}{2}$ to 3 ampères at a potential of 5 to 6 volts is used. Heat is evolved during the reaction. The products usually separate as sulphates, either at once or on remaining in a cool place. If the product is very soluble in sulphuric acid, it is precipitated on the addition of water. The following results were obtained.

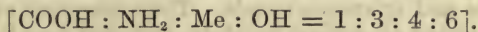
Nitrobenzene yields paramidophenol sulphate. Orthonitrotoluene yields an amidocresol, which is easily soluble in alkali, and gives a violet coloration with ferric chloride; the author is engaged in the further examination of this compound. Metadinitrobenzene yields orthoparadiamidophenol, which is identical with the compound obtained from orthoparadinitrophenol. Orthoparadinitrotoluene yields *diamidocresol*, $C_6H_2Me(NH_2)_2 \cdot OH$ [1 : 4 : 6 : 3]. It crystallises in broad needles, is unstable, and melts at 170° with a brown coloration.

The *sulphate* crystallises in colourless needles, turns brown on exposure to air, and gives an intense violet coloration with ferric chloride, dichromate, nitric acid, and bromine water.

Metanitraniline yields orthoparadiamidophenol. Orthonitroparatomuidine yields the diamidocresol (m. p. 170°) described above, which is also obtained by the electrolytic reduction of paranitroorthotoluidine.

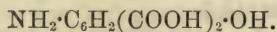
Metanitrobenzoic acid yields amidosalicylic acid [$\text{COOH} : \text{NH}_2 : \text{OH} = 1 : 3 : 6$]; this crystallises in long, colourless needles, is not altered by exposure to air, and is decomposed by heat into amidophenol and carbonic anhydride. The *sulphate* crystallises in broad, colourless needles.

Metanitroparatoluic acid yields *amidocresotic acid*,



The *sulphate* crystallises with water in colourless needles which effloresce on exposure to air; it gives a violet coloration with ferric chloride. By displacing the amido-group in amidocresotic acid by chlorine, bromine, and iodine, the following compounds were obtained: *chlorocresotic acid* crystallises in white plates, and melts at $203\text{--}204^{\circ}$; *bromocresotic acid* crystallises in silvery leaflets, and melts at 211° ; *iodocresotic acid* crystallises in short needles, and melts at 227° .

Nitroterephthalic acid yields the *amidohydroxy-acid*,



It separates in beautiful crystals from hot water, gives a reddish-brown coloration with ferric chloride, and when treated with nitrous acid yields a sparingly soluble diazo-compound, which crystallises in short, brownish-red needles.

Nitroisophthalic acid also yields an amidohydroxy-acid, which crystallises with H_2O in colourless needles, and is dehydrated by heating at 180° .

1:4-Nitronaphthalenesulphonic acid yields a compound which crystallises from water in silvery plates, and reduces ammoniacal silver solution in the cold. It is either an amidonaphtholsulphonic acid or an amidosultone.

Paranitrotoluene behaves in quite a different way from the above compounds, and yields a condensation product which the author believes to be *nitroamidoorthobenzytoluene*, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NO}_2$. It forms orange-red crystals, and melts at 119° . The *sulphate* crystallises in beautiful, white needles, which reddened on exposure to air. The *acetyl compound*, $\text{NO}_2 \cdot \text{C}_{14}\text{H}_{12} \cdot \text{NHAc}$, crystallises in short, yellow needles, and melts at 174° . The *benzoyl compound* crystallises in silky needles, and melts at 185° . The *thiocarbamide*, obtained by warming an alcoholic solution of the base with phenyl isothiocyanate, crystallises in white leaflets, and melts at 167° . The base combines with benzaldehyde to yield a *benzylidene derivative*, $\text{NO}_2 \cdot \text{C}_{14}\text{H}_{12} \cdot \text{N} : \text{CHPh}$, which crystallises in broad, colourless needles, and melts at 194° . The *phenol*, $\text{NO}_2 \cdot \text{C}_{14}\text{H}_{12} \cdot \text{OH}$, obtained from the base in the usual way through the diazo-compound, crystallises in yellow needles, and melts at 117° . The *dibromide*, $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2\text{Br}_2$, crystallises in colour-

less leaflets, and melts at 150° . When the nitroamido-base is reduced with stannous chloride and hydrochloric acid, it yields a *diamine*. The latter boils at 380° , melts at $59-60^{\circ}$, and crystallises in long needles. The *sulphate* crystallises in colourless needles. The *diacetyl derivative*, $C_{14}H_{12}(NHAc)_2$, melts at 220° . The *phenol*, $C_{14}H_{12}(OH)_2$, obtained in the usual way, crystallises in long needles, and melts at $138-139^{\circ}$.
E. C. R.

Action of Sodium Sulphite on Salts of Amidophenols. By A. LUMIÈRE and A. SEYEWITZ (*Compt. rend.*, **116**, 1202—1205).—Amidophenols are difficult to isolate from their salts, by reason of the energy with which they absorb oxygen from the air, and this is true also of diamidophenols and triamidophenols. The separation can, however, be effected by means of sodium sulphite, provided that the particular amidophenol is insoluble in a solution of sodium sulphite and is so feebly basic that it will not combine with sulphurous acid.

A concentrated solution of paramidophenol hydrochloride, when treated with a saturated solution of sodium sulphite, yields the base in white, crystalline, nacreous plates which, after being dried at $30-40^{\circ}$, melt at 184° . The reaction is practically quantitative. The product is, however, liable to become slowly black when exposed to the air, but this can be prevented by using for precipitation and the washing of the precipitate a solution of sodium sulphite which is slightly acid to phenolphthaleïn.

Diamidophenol must be precipitated in a saturated solution of sodium sulphite containing some undissolved crystals of the salt and mixed with sufficient sulphurous acid to make it slightly acid to phenolphthaleïn. The hydrochloride is dissolved in 5 parts of this solution and powdered sodium sulphite added until it no longer dissolves; the diamidophenol then gradually separates. It melts at $78-80^{\circ}$ and alters very rapidly when exposed to air, but can be kept in flasks filled with sulphurous anhydride. It is somewhat soluble in water, alcohol, and acetone, and slightly soluble in ether, benzene, and chloroform. It dissolves very readily in either acid or alkalis, and all its solutions oxidise when exposed to air. Oxalic acid converts the base into a white powder, insoluble in water and stable when exposed to air. This product is probably diamidophenol oxalate, and it is under investigation.

When a concentrated aqueous solution of triamidophenol hydrochloride is mixed with a saturated solution of sodium sulphite, an abundant, white precipitate is formed, which is very slightly soluble in cold water or in alcohol. This product forms white plates which melt at $120-121^{\circ}$ with evolution of sulphurous anhydride. It dissolves in acids with evolution of sulphurous anhydride, and it also dissolves in alkalis. All the solutions oxidise when exposed to air. The compound has the composition $C_6H_4(NH_2)_3 \cdot OH, H_2SO_3$, and its formation is due to the fact that triamidophenol is a more energetic base than amidophenol or diamidophenol.
C. H. B.

Cinnamylamine and its Derivatives. By T. POSNER (*Ber.*, **26**, 1856—1865).—*Cinnamylphthalimide*, $CHPh \cdot CH \cdot CH_2 \cdot N \cdot C_8H_4O_2$, is ob-

tained by heating cinnamyl chloride with potassium phthalimide at 160°. It crystallises in small, white needles, and melts at 153°.

Cinnamylphthalamic acid, $C_9H_9 \cdot NH \cdot CO \cdot C_6H_4 \cdot COOH$, is obtained by dissolving the preceding compound in warm potassium hydroxide and precipitating with hydrochloric acid. It melts at 132°. The *silver* salt is a white, flocculent precipitate which turns brown on exposure to light.

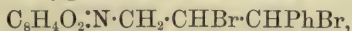
Cinnamylamine, $CHPh \cdot CH \cdot CH_2 \cdot NH_2$, is obtained, together with phthalic acid and cinnamylphthalimide, by heating the preceding compound with concentrated hydrochloric acid in a reflux apparatus. It is also obtained as hydrochloride, together with di- and tri-cinnamylamine hydrochlorides, by heating cinnamyl chloride with alcoholic ammonia at 100°. The product is shaken with equal parts of water and ether; the cinnamylamine hydrochloride dissolves in the water; the ether extracts the resinous products and the di- and tri-styrylamine hydrochlorides remain undissolved. Cinnamylamine is a colourless, oily liquid, boils at 235–237° under 775 mm. pressure, is sparingly volatile with steam, and has an odour resembling that of benzylamine. It absorbs carbonic anhydride from the air with great readiness. The *hydrochloride* crystallises in white, silky needles, and melts at 210°. The *picrate* melts at 173°. The *platinochloride* melts at 205–207°.

Cinnamylbenzamide, $CHPh \cdot CH \cdot CH_2 \cdot NHBz$, crystallises in needles, and melts at 94–95°.

Cinnamylphenylthiocarbamide separates in beautiful, white crystals, and melts at 116–118°.

Cinnamylphenyl-ψ-thiocarbamide, $NHPh \cdot C \begin{smallmatrix} \swarrow N-CH_2 \\ \searrow S \cdot CHPh \end{smallmatrix} > CH_2$ or $NHPh \cdot C \begin{smallmatrix} \swarrow N \cdot CH_2 \\ \searrow S \cdot CH \cdot CH_2Ph \end{smallmatrix}$, is obtained by heating the preceding compound with fuming hydrochloric acid at 100° for three hours, and treating the product with alkali. It crystallises in beautiful, colourless prisms, and melts at 205°. The *hydrochloride* and *hydrobromide* do not crystallise, and are insoluble in the presence of the free acid. The *picrate* crystallises in beautiful yellow needles, and melts at 200°. The *platinochloride* is a bright yellow, microcrystalline precipitate, and melts at 182° with decomposition.

Two isomeric *cinnamylphthalimide dibromides*,



are obtained by adding bromine to a well-cooled solution of styrylphthalimide in chloroform. They are separated by fractional crystallisation from ethylic acetate; the less soluble compound crystallises in white needles, and melts at 165°, whilst the more soluble compound forms colourless, nodular aggregates, and melts at 117°.

Dicinnamylamine, $NH(CH_2 \cdot CH \cdot CHPh)_2$, is obtained as described above. It is separated from the tricinnamylamine by means of ethylic acetate, in which it is sparingly soluble. It is a colourless oil, and boils at a very high temperature. The *hydrochloride* crystallises in large, white scales, melts at 223° with a brown coloration, and when heated with amylic nitrite yields a colourless oil. The *picrate* crystallises in long, yellow needles, and melts at 126°.

Tricinnamylamine, $N(CH_2 \cdot CH \cdot CHPh)_3$, forms long, colourless needles, and melts at 89° . The *hydrochloride* melts at 101° . The *methiodide* crystallises in six-sided columns, melts at $129-130^\circ$, and colours yellow on exposure to air. The corresponding *chlorine compound* is obtained by treating an alcoholic solution of the iodide with excess of freshly prepared silver chloride. It melts at 166° . The *platinochloride*, $C_{36}H_{60}N_2PtCl_6$, is an insoluble, yellow precipitate, and melts at 195° . E. C. R.

Action of Nitrous acid on Ketoamines. By A. ANGELI (*Ber.*, 26, 1715—1719).—Nitrous acid reacts quite generally with the amido-group, but it seems that the diazo-compound primarily formed is only stable when this group is directly connected with a group of negative character (for example, phenyl), or, as in the case of diazo-compounds of amido-acids, is joined to a carbon atom which is itself joined to a negative group. The ketoamines, containing the group $-CO \cdot CH(NH_2)-$, also satisfy this last condition, and we might expect them to behave like the amido-acids, and yield diazo-derivatives. This they actually do; amidoacetophenone hydrochloride, when it is mixed with sodium nitrite in aqueous solution, and acetic acid is added to the cooled mixture, yields *monoketazophenylglyoxal* or *diazoacetophenone*, $CPhO \cdot CH \cdot N_2$, which forms lustrous, yellow needles melting at 50° ; amidocamphor hydrochloride in like manner yields *monoketazocamphorquinone*, $C_8H_{14} < \begin{smallmatrix} CO \\ C:N_2 \end{smallmatrix}$; this forms yellow crystals, melts at 74° , and gives with benzaldehyde in toluene solution a substance melting at 170° , probably benzoylcamphor. C. F. B.

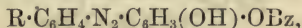
Action of Diazobenzeneimide on Methylic Acetylenedicarbonylate. By A. MICHAEL (*J. pr. Chem.* [2], 48, 94—95).—When these compounds in equivalent proportion are mixed in ether and exposed to sunlight, or heated in a sealed tube, a white compound, $C_{12}H_{11}N_3O_4$, which crystallises in needles and melts at $126-127^\circ$, is formed. By treating this ethereal salt with alcoholic potash, the corresponding acid was isolated and was found to melt at $149-150^\circ$ with decomposition. The reaction is comparable with those observed by Buchner (*Abstr.*, 1889, 694; this vol., i, 432) and by v. Pechmann (*Abstr.*, 1891, 1115). A. G. B.

Nitrohydroxy- and Nitroamido-azo-compounds. By E. TÄUBER (*Ber.*, 26, 1872—1876).—Nitroamidoazosulphonic acids are easily obtained by heating nitrohydroxyazosulphonic acids with 20—25 per cent. ammonia at $150-160^\circ$ for 16 hours. The nitrohydroxyazosulphonic acids are obtained by dissolving hydroxyazosulphonic acids in concentrated sulphuric acid, adding the theoretical quantity of potassium nitrate, and then pouring the mixture into water.

The author has prepared the following compounds by this method:—Metanitroparahydroxyazobenzeneparasulphonic acid, metanitroparahydroxyazobenzenemetasulphonic acid, metanitroparamidoazobenzeneparasulphonic acid, metanitroparamidoazobenzenemetasulphonic acid,

and the homologous compounds derived from the toluidinesulphonic acids. E. C. R.

Azo-derivatives of Quinol. By O. N. WITT and E. S. JOHNSON (*Ber.*, 26, 1908—1912).—These cannot be prepared directly by the action of a diazo-compound on quinol, because of the reducing power of the latter. If, however, it be converted in the usual way into *benzoylquinol*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$ (flat, colourless, glassy needles, melting at $162\text{--}163^\circ$), this substance, when treated with a diazo-compound, $\text{R}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{Cl}$, yields an azo-colouring matter,



and from this benzoate, by hydrolysis with alcoholic potash, the corresponding azo-derivative, $\text{R}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$, of quinol itself is obtained.

Anilineazoquinol, $\text{N}_2\text{Ph}\cdot\text{C}_6\text{H}_3(\text{OH})_3$, forms red needles melting at $145\text{--}148^\circ$, the *benzoate*, orange-red crystals melting at $110\text{--}112^\circ$. *Paratoluidineazoquinol*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$, forms greenish-black needles, red by transmitted light, melting at $168\text{--}170\cdot5^\circ$; the *benzoate* lustrous, silky, orange-yellow needles melting at $113\text{--}115\cdot5^\circ$. *Paranitranilineazoquinol*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$, forms large, black tables with greenish, adamantine lustre, and decomposes at $185\text{--}190^\circ$; the *benzoate* forms lustrous, brownish-red needles melting at $195\text{--}197^\circ$. *Sulphanilic acid azoquinol*, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$, was obtained in the form of its *sodium salt*, a reddish-brown, crystalline precipitate; the *sodium* and *barium salts* of the *benzoate* form golden-yellow crystals. C. F. B.

Action of Ethylenic Bromide on Phenylhydrazine. By C. D. HARRIES (*Ber.*, 26, 1865—1867).—When phenylhydrazine and ethylenic bromide, dissolved in alcohol, are heated on the water-bath for 10 hours, a crystalline product is obtained which melts at $179\text{--}180^\circ$, and is a mixture of two isomeric *diethylenetriphenylhydrazines*, $(\text{C}_2\text{H}_4)_2\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5(\text{NHNHPh})_2$.

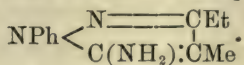
The less soluble isomeride crystallises in beautiful, long, lustrous prisms, reduces Fehling's solution and silver solution when warmed, and is a weak base. It dissolves in nitric acid with a characteristic deep-blue colour, and, when reduced with zinc dust and hydrochloric acid, yields ammonia and aniline. The *platinochloride* crystallises in thick, dark red prisms.

The more soluble isomeride forms beautiful crystals, melts at $167\text{--}168^\circ$, and has properties similar to the preceding, but is more soluble.

If the mixture of phenylhydrazine, ethylenic bromide, and alcohol is heated too rapidly or for too long a time, a deep brown solution is obtained which deposits a crystalline compound melting at $179\text{--}180^\circ$. It forms long, bright-brown spears, and does not give a blue solution with nitric acid. E. C. R.

The so-called Hydrazone of Cyanacetone. By L. BOUVEAULT (*Bull. Soc. Chim.* [3], 9, 375—377).—Burns (this vol., i, 315) has

described the compound obtained by the action of phenylhydrazine on imidoacetylacetonitrile as cyanacetone hydrazone. The author points out that this compound has none of the properties of a hydrazone, in which respect it resembles the compound which he obtained (Abstr., 1891, 52) when submitting propionylpropionitrile to a similar treatment. He seeks to account for the irregular behaviour of these hydrazones by postulating an intramolecular transposition whereby the hydrazone becomes an amido-pyrazole; $N_2HPh:CEt \cdot CHMe \cdot CN$, for example, becoming



If this view be correct, it will be found that these compounds distil unchanged at the ordinary pressure, and that they behave as primary aromatic bases towards nitrous acid, yielding salts of diazo-derivatives.

A. G. B.

Stereoisomerism of the Benzhydroxamic acids. By W. LOSSEN (*Ber.*, 26, 1818—1819).—A rejoinder to Werner (this vol., i, 510).

The Two Isomeric Benzyl Derivatives of Nitroso- β -benzylhydroxylamine. By R. LINDNER (*Annalen*, 275, 133—144).—The sodium salt of nitroso- β -benzylhydroxylamine melts at 233—234° with decomposition, and the silver salt melts at 108—109° with decomposition. On benzylating the sodium salt as described by Behrend and König (Abstr., 1891, 1035), the compound melting at 58—59° is obtained, together with oily products and a small quantity of the isomeric compound melting at 73—74°. The latter was obtained by Behrend and König (*loc. cit.*) by the action of nitrous acid on α -dibenzylhydroxylamine. Both compounds have the same molecular weight, give Liebermann's reaction, and are insoluble in alkalis. When an ethereal solution of the compound melting at 73—74° is treated with hydrogen chloride, α -dibenzylhydroxylamine is obtained, whereas the compound melting at 58—59° remains unaltered under these circumstances; when, however, the latter is heated in a sealed tube at 120—130° with hydrochloric acid, β -benzylhydroxylamine, benzyl chloride, and nitrogen are formed. Both compounds give benzylamine and benzylic iodide on reduction with hydriodic acid and phosphorus.

The author concludes from these experiments that the compound melting at 58—59° has the constitution represented by one of the formulæ $\begin{array}{c} C_7H_7 \cdot N \\ | \\ C_2H_7 \cdot N \end{array} > O$ or $C_7H_7 \cdot NO : N \cdot OC_2H_7$, whilst the compound melting at 73—74° is a true nitrosamine.

A. R. L.

Paramagenta. By A. MIOLATI (*Ber.*, 26, 1788—1790).—Three different views are at present held as to the nature of the change which takes place when pararosaniline is converted into one of its coloured salts. The oldest supposition is that union takes place between the methane carbon atom and one of the nitrogen atoms,

the latter also combining with the acid, the hydrochloride having, for example, the constitution $C(C_6H_4 \cdot NH_2)_2 < \begin{matrix} C_6H_4 \\ | \\ NH, HCl \end{matrix}$. Nietzki, on the other hand, regards the coloured salts as derivatives of substituted quinonimide compounds, and ascribes to the hydrochloride the formula $(C_6H_4 \cdot NH_2)_2 C : C_6H_4 \cdot NH, HCl$, whilst Rosenstiel and v. Richter suggest that it may be formed by the substitution of chlorine for the hydroxyl group in pararosaniline, as shown by the formula $CCl(C_6H_4 \cdot NH_2)_3$.

If the latter supposition is correct, the salt, like other similar tertiary chlorides, must be a non-electrolyte, whereas, if it has either of the first two formulæ, it must conduct electricity in the same manner as the metallic salts. Experiment has shown that a solution of the salt does conduct electricity, its molecular conductivity being about 46.5. Pararosanine is therefore a stronger base than quinaldine, and its salts undergo electrolytic dissociation in aqueous solution; so that the formula proposed by Rosentiel and v. Richter cannot be correct. Between the other two formulæ this method is unable to decide.

H. G. C.

A New Series of Colouring Matters. By A. TRILLAT (*Compt. rend.*, 116, 1382—1385).—Formaldehyde reacts readily with aniline, yielding anhydroformaldehydaniline, $C_6H_5N : CH_2$ (this vol., i, 439). When paraleucaniline is dissolved in dilute alcohol and treated with formaldehyde, two of the phenyl groups undergo a similar transformation, and the product is a white powder which melts at 198° , turns blue when exposed to air, dissolves in acids, and is decomposed by alkalis. If the reaction takes place in presence of an acid, the change goes no further, but the product is insoluble in acids.

Rosaniline, with formaldehyde, yields a violet colouring matter similar to that obtained by Lauth from rosaniline and acetaldehyde. It dissolves readily in acids, but although the dye resists the action of soap fairly well when applied to fabrics, it is not stable. In order to obtain this product, 50 grams of rosaniline is dissolved in 500 c.c. of water acidified with 25 grams of sulphuric acid, and the warm liquid is mixed with 25 grams of a 40 per cent. solution of formaldehyde. The liquid is then heated until its colour undergoes no further change. The sulphone derivative of rosaniline yields a similar product, which, however, is redder in colour, and stable when exposed to light, but does not resist washing so well.

Safranine readily yields an analogous product when mixed with formaldehyde in presence of an excess of hydrochloric acid. It has the composition $CH_2 : N \cdot C_6H_3 \cdot N_2 Cl (C_6H_4)_2 N : CH_2$, forms crystals with a very brilliant metallic lustre, dyes silk, wool, and cotton without a mordant, and the colour resists the action of soap and hot water in a very remarkable manner.

Diamidophenylacridine, $C_{19}H_5N_3$, yields an orange derivative, $C_{19}H_{11}N_3(CH_2)_2$, only slightly soluble in acids, and similar to chrys-aniline in its tinctorial properties.

Amidoalizarine also reacts with formaldehyde in presence of a

large excess of sulphuric acid, and yields a dye with a somewhat more violet shade.

When chrysoidine, sulphuric acid, and formaldehyde are heated together on a water-bath, a new colouring matter is obtained which dyes cotton brick-red without a mordant. From analogy, it would seem to have the constitution $C_6H_5N \cdot NC_6H_5 : (N \cdot CH_2)_2$.

20 grams of Congo-red, dissolved in 300 grams of water, and heated on a water-bath with 8 grams of formaldehyde solution, yields a yellow colouring matter with the same tinctorial properties as the parent substance. Bismark-brown, the indulines, &c., yield analogous products.
C. H. B.

Derivatives of Orthamidobenzamide. By H. FINGER (*J. pr. Chem.*, [2], 48, 92—93; compare Abstr., 1888, 948).—*Orthamidobenzethyleneamide*, $C_2H_4(NH \cdot CO \cdot C_6H_4 \cdot NH_2)_2$, obtained from isatoic acid and ethylenediamine, crystallises in pale, rose-coloured, lustrous laminæ, and melts at 245° . Treatment with potassium nitrite and an acid converts it into *ethylenebenzazimide*, $C_2H_4(N < \begin{smallmatrix} N:N \\ CO \end{smallmatrix} > C_6H_4)_2$, which crystallises in yellowish-white, lustrous needles, and melts at 216° .

Orthamidobenzhydrazine, $NH_2 \cdot C_6H_4 \cdot CON_2H_5$, is prepared by adding isatoic acid to a hot solution of hydrazine sulphate and potassium hydroxide; it crystallises in monoclinic prisms and needles, and melts at 121° ; it reduces Fehling's solution. With benzaldehyde, it forms a yellow, crystalline *condensation product*, melting at 158 — 159° .

A. G. B.

Anhydriisation of Oximido-acids. By A. HANTZSCH and A. MIOLATI (*Zeit. physikal. Chem.*, 11, 737—750).—Oximido-acids which have the NOH group in the β - or γ -position exist as a rule only in the form of internal anhydrides—the oxazolones, which when treated with alkalis are converted more or less readily into the alkaline salts of the original acids. The authors have studied the rate at which this splitting of the oxazolone ring takes place, in order to ascertain the effect of various hydrocarbon radicles in the molecule in furthering or preventing the formation of internal anhydrides.

The anhydrides of the β -oximido-acids are so readily attacked by alkalis that the rate at which they are converted into salts cannot be measured even at extreme dilutions. The best results were obtained with the anhydrides of γ -oximido-acids derived from phthalic acid, which are of the type $C_6H_4 < \begin{smallmatrix} CR:N \\ CO \cdot O \end{smallmatrix} >$. As these anhydrides are

insoluble in cold water, the measurements were made in 90 per cent. alcohol. The temperature of experiment was 25° , and the dilution was 1/200 normal. The following table contains the velocity constants found:—

R.	Const.	R.	Const.
Isopropyl	0.52	Benzyl	1.07
Normal propyl	0.65	Methyl	1.12
Ethyl	0.74	Phenyl	2.59

From these numbers, it appears that the phenyl group protects the

oxazolone ring much less than the alkyl radicles, the protecting influence of which increases with their molecular weight and with the number of methyl groups contained in them. J. W.

Phenyldithiobiuret. By E. FROMM (*Annalen*, **275**, 20—49).—Phenyldithiobiuret, when quite pure, melts at 184°. The preparation of α -phenyldithiodimethylketuret, which is now stated to melt at 236°, and of its dibenzyl derivative have been already described (Abstr., 1892, 844). Dibenzylid imidodithiooxalate (*loc. cit.*) yields biuret on treatment with alcoholic ammonia.

α -Phenyldithiophenylalduret, $\text{NPh}\cdot\text{C}(\text{SH})\cdot\text{N}<\begin{smallmatrix} \text{C}(\text{SH}) \\ \text{CHPh} \end{smallmatrix}>\text{N}$, is obtained by treating molecular proportions of α -phenyldithiobiuret and benzaldehyde with dry hydrogen chloride; it forms lustrous leaflets, melts at 227°, and yields a *dibenzyl* derivative which crystallises in white needles, and melts at 112°.

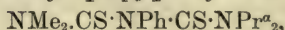
When α -phenyldithiobiuret is oxidised with alcoholic iodine, ferric chloride and hydrochloric acid, with potassium ferricyanide, ammonium chloride, and ammonia, or with hydrogen peroxide and hydrochloric acid, a weak base, $\text{C}_8\text{H}_7\text{N}_3\text{S}_2$, named by the author *thiuret*, is obtained; it crystallises both from water and from alcohol with solvent of crystallisation which is only eliminated by keeping it over concentrated sulphuric acid in a vacuum. The *hydriodide*, $\text{C}_8\text{H}_7\text{N}_3\text{S}_2\cdot\text{HI}$, crystallises from methyl or ethyl alcohol with 1 mol. of the solvent, and melts at 104° and 110° respectively with decomposition. When this salt is crystallised from concentrated hydrochloric acid, the hydrochloride is obtained; it crystallises from water with $3\text{H}_2\text{O}$, and from alcohol with 1EtOH , the melting point being in the latter case 214°. The *hydrobromide* melts at 253°; the *borate* at 144°; the *salicylate* at 76°; the *orthocresotate* at 75°; and the *paraphenylsulphonate* at 215°. Thiuret is converted into α -phenyldithiobiuret on reduction with zinc and hydrochloric acid; when distilled with 10 per cent. soda, it yields α -phenyldithiobiuret, aniline, and ammonia, whilst heating in a sealed tube at 165° with concentrated hydrochloric acid decomposes it into hydrogen sulphide, sulphur, carbonic anhydride, ammonia, and v. Hofmann's methenylamidophenylmercaptamine, $\text{C}_6\text{H}_4<\begin{smallmatrix} \text{S} \\ \text{N} \end{smallmatrix}>\text{CNH}_2$ (Abstr., 1880, 884), which, according to the author, melts at 132°. The author, therefore, regards the formula $\text{NPh}\cdot\text{C}<\begin{smallmatrix} \text{S}\cdot\text{S} \\ \text{NH} \end{smallmatrix}>\text{C}\cdot\text{NH}_2$, as the most probable for thiuret. A. R. L.

Penta-substituted Dithiobiurets. By O. BILLETER (*Ber.*, **26**, 1681—1688).—*Dimethylphenylthiocarbamide*, $\text{NMe}_2\cdot\text{CS}\cdot\text{NHPh}$, prepared from dimethylamine and phenylthiocarbimide, crystallises in large, colourless needles, and melts at 132—132·5°. *Diethylphenylthiocarbamide*, $\text{NEt}_2\cdot\text{CS}\cdot\text{NHPh}$, obtained from diethylamine and phenylthiocarbimide, does not crystallise. *Dipropylphenylthiocarbamide*, $\text{NPr}^a_2\cdot\text{CS}\cdot\text{NHPh}$, prepared from dipropylamine and phenylthiocarbimide, is deposited in needles which melt at 66°. *Diamylphenylthiocarb-*

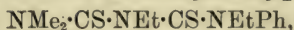
amide, $N(C_5H_{11})_2 \cdot CS \cdot NPh$, obtained from diamylamine and phenylthiocarbimide, crystallises in lustrous plates, and melts at $72-72.3^\circ$. Dimethylethylthiocarbamide, $NMe_2 \cdot CS \cdot NHEt$, prepared from dimethylamine and ethylthiocarbimide, forms colourless needles melting at $37-37.5^\circ$. Dipropylethylthiocarbamide, $NPr^a_2 \cdot CS \cdot NHEt$, obtained from dipropylamine and ethylthiocarbimide, and diethylphenylthiocarbamide, $NEt_2 \cdot CS \cdot NPh$, prepared from diethylamine and phenylthiocarbimide, are very similar in crystalline form, and melt at $34-34.5^\circ$.

Dimethylthiocarbamine chloride, $NMe_2 \cdot CS \cdot Cl$, crystallises in yellow prisms melting at 42° . Diethylthiocarbamine chloride, $NEt_2 \cdot CS \cdot Cl$, is deposited in yellow prisms, melts at $46.2-46.5^\circ$, and boils at 108° under a pressure of 10 mm. Dipropylthiocarbamine chloride, $NPr^a_2 \cdot CS \cdot Cl$, is a yellow liquid boiling at $124.2-124.3^\circ$ under a pressure of 10 mm. Diamylthiocarbamine chloride, $N(C_5H_{11})_2 \cdot CS \cdot Cl$, resembles the preceding compound and boils at $155-170^\circ$ under 16 mm. pressure. These compounds were prepared in the manner previously described (Abstr., 1887, 822).

Dimethylethylidiphenyldithiobiuret, $NMe_2 \cdot CS \cdot NPh \cdot CS \cdot NEtPh$, is prepared by heating dimethylthiocarbamine chloride with ethylthiocarbanilide, or ethylphenylthiocarbamine chloride with dimethylphenylthiocarbamide, and is deposited in pale-yellow isometric crystals melting at 98.8° . Dimethyldipropylphenyldithiobiuret,



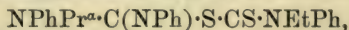
is formed either from dimethylthiocarbamine chloride and dipropylphenylthiocarbamide, or from dipropylthiocarbamine chloride and dimethylphenylthiocarbamide; it is deposited in almost colourless crystals melting at $80.5-81^\circ$. Dimethyldiethylphenyldithiobiuret,



is prepared from dimethylthiocarbamine chloride and diethylphenylthiocarbamide, or from ethylphenylthiocarbamine chloride and dimethylphenylthiocarbamide, and crystallises in yellow needles or prisms melting at $113.5-114^\circ$.

By the action of the above-mentioned thiocarbamine chlorides on the thiocarbamides at ordinary temperatures in chloroform solution and treatment of the products with potash, two compounds are obtained isomeric with the dithiobiurets, which the author proposes to term pseudodithiobiurets; they are somewhat unstable, and, on heating, are readily converted into the corresponding dithiobiuret.

α -Ethylpropyltriphenylpseudodithiobiuret,



is prepared from ethylphenylthiocarbamine chloride and propylthiocarbanilide, and crystallises in yellow rhombohedra, melting at $68.2-69^\circ$. The hydrochloride is deposited in quadratic crystals.

β -Ethylpropyltriphenylpseudodithiobiuret, is formed from propylphenylthiocarbamine chloride and ethylthiocarbanilide, and is resinous; like the preceding compound, it is converted into ethylpropyltriphenyldithiobiuret (*loc. cit.*) on heating. α -Dimethylethylidiphenylpseudodithiobiuret, $NEtPh \cdot C(NPh) \cdot S \cdot CS \cdot NMe_2$, is prepared from dimethylthiocarbamine chloride and ethylthiocarbanilide and crystal-

lises in slender needles melting at 89.8° . The *hydrochloride* is deposited in yellow, orthorhombic crystals. β -Dimethylethyldiphenyl-pseudodithiobiuret crystallises in yellow prisms, and melts at 91.2° . The *hydrochloride* is crystalline. Both these bases are converted into the ordinary dithiobiuret (m. p. 98.8° ; see above) by heating for a short time on the water-bath.

The formulæ given to the above compounds can only be regarded as provisional; the author does not attempt to distinguish by means of formulæ between the two modifications of the pseudo-derivatives, nor does he consider that there is evidence to show that they are stereoisomeric.

J. B. T.

Benzoyl Derivatives of Benzoylacetone.¹ By L. CLAISEN (*Ber.*, 26, 1879—1881).—When the sodium salt of benzoylacetone, prepared by treating benzoylacetone with sodium ethoxide, is treated with benzoic chloride, a compound, $C_{17}H_{14}O_3$, is obtained which is similar to the dibenzoylacetone obtained by Fischer and Bülow (*Ber.*, 18, 2133). It melts at 101 — 102° , and is not appreciably attacked by sodium in ethereal solution. It is, however, of strongly acid character, and dissolves easily in dilute soda forming a yellow solution. With copper acetate, it gives a bright blue copper salt, and with ferric acetate, a yellowish-brown iron salt. By repeated crystallisation from alcohol, it is converted into an isomeric compound which melts at 109 — 112° .

E. C. R.

Orthiodobenzoic acid and some of its Derivatives. By W. WACHTER (*Ber.*, 26, 1744—1745).—The author gives an improved method for the preparation of orthiodobenzoic acid from anthranilic acid. The melting point of the pure acid is 162° . The *methylic salt* boils at 167° (25 mm.), and the *ethylic salt* at 275° (760 mm.). The *chloride* forms yellow crystals, melting at 35 — 40° ; the *amide*, *anilide*, *ortho-* and *para-toluidides*, and the *phenylhydrazide* are crystalline substances prepared from the chloride. *Orthiodobenzophenone* is a dark coloured oil, which solidifies partially after a time. Its *oxime* melts at 150° . On treatment with hydroxylamine in alkaline solution, orthiodobenzophenone is converted in the cold into phenyl-indoxazen.

A. H.

Iodoxybenzoic and Iodosobenzoic acids. By C. HARTMANN and V. MEYER (*Ber.*, 26, 1727—1732; compare *Abstr.*, 1892, 1460; this vol., i, 506).—Iodoxybenzoic acid, $IO_2 \cdot C_6H_4 \cdot COOH$, is formed, together with orthiodobenzoic acid, by the action of potassium permanganate on an alkaline solution of iodosobenzoic acid. The pure acid, obtained by acidifying a solution of one of the salts, forms white needles which gradually become coloured red on exposure to light, and decompose with a sharp report when heated to 233° . It is a much stronger acid than the iodoso-derivative, reddens litmus strongly, decomposes carbonates, and has an intensely acid taste. It reacts quantitatively with acid solutions of potassium iodide, iodosobenzoic acid being formed and iodine liberated. The *silver salt*, with $\frac{1}{2}H_2O$, crystallises from hot water, in which it is only slightly soluble, in groups of small, yellowish plates, and explodes on heating. The

barium and *calcium* salts are amorphous, and soluble in water, whilst the *lead* and *mercuric* salts are insoluble. The acid is decomposed by boiling aqueous soda into sodium iodate and benzoate; no salicylic acid being formed. It has been found impossible to prepare ethereal salts of the acid; methyl alcohol and hydrochloric acid produce *iodosobenzoic anhydride*, $(\text{IO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO})_2\text{O}$, which may also be obtained by the action of the same reagents on iodosobenzoic acid itself; it is a white, crystalline substance, which melts at $219\text{--}220^\circ$, and is insoluble in sodium carbonate solution. Ethyl alcohol and hydrochloric acid, on the other hand, yield only orthiodobenzoic acid, and the ethylic salt of this acid is formed by the action of ethylic iodide on silver iodoxybenzoate. Phosphoric chloride acts violently on the acid, causing it to deflagrate, but in solution in phosphorus oxychloride iodosobenzoic acid and its anhydride are formed. Free iodoxybenzoic acid gives characteristic colour reactions with aniline, aniline hydrochloride, and phenol, and is decomposed by boiling sulphuric acid with liberation of iodine.

Iodosobenzoic acid reacts with isobutylamine in acetic acid solution in the same way as with ethylamine, orthiodobenzoic acid being formed.
A. H.

Iodoso- and Iodoxy-derivatives of Metanitropariodobenzoic acid. By L. S. ALLEN (*Ber.*, 26, 1739—1744; compare foregoing abstracts).—*Para-iodosometanitrobenzoic acid* (this vol., i, 508) is a fiery yellow-coloured, amorphous powder, resembling lead chromate in appearance. It has no definite melting point, but decomposes and becomes liquid from 190° to 205° . It dissolves to a very slight extent in glacial acetic acid, but is insoluble in all other ordinary solvents. The acid is sufficiently strong to decompose carbonates, and it forms amorphous salts with barium, silver, lead, copper, and other of the heavy metals. With acid solutions of potassium iodide, it reacts in the characteristic manner, para-iodometanitrobenzoic acid being formed, and, like ortho-iodosobenzoic acid, is simply reduced by the action of alcohol and hydrochloric acid, no ethereal salt being produced. Caustic soda decomposes it into sodium metanitro- and pariodometanitro-benzoates and iodate.

Pariodoxymetanitrobenzoic acid, $\text{IO}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{COOH}$, is formed by the action of potassium permanganate in acid solution on the iodoso-acid. It is a yellow powder, slightly soluble in hot alcohol and water. When slowly heated, it commences to decompose at 180° , but when rapidly heated in a melting-point tube, it explodes violently.

Metaiodo-orthobenzoic acid does not yield an iodoso-derivative when treated by the usual methods.
A. H.

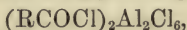
Metallic Compounds of the Benzene Series. By G. PERRIER (*Compt. rend.*, 116, 1298—1300).—Benzoic chloride, when boiled with aluminium chloride in presence of carbon bisulphide, yields the compound $(\text{PhCOCl})_2\text{Al}_2\text{Cl}_6$ in large, colourless lamellæ, which readily alter when exposed to air, and yield aluminium chloride, hydrogen chloride, and benzoic acid when treated with water.

If a mixture of this compound with diphenyl is boiled with carbon bisulphide, hydrogen chloride is evolved, and, on cooling, the compound $(C_6H_5 \cdot CO \cdot C_6H_4 \cdot C_6H_5)_2 Al_2 Cl_6$ separates in large, yellow needles, identical with those obtained by heating benzoyldiphenyl with aluminium chloride in presence of carbon bisulphide. When treated with water, the compound yields aluminium chloride and parabenzoyldiphenyl.

Retene, under the same conditions, yields red crystals of the compound $(C_6H_5 \cdot CO \cdot C_{18}H_{17})_2 Al_2 Cl_6$, and β -naphthol yields the golden-yellow compound $(C_6H_5 \cdot CO \cdot C_{10}H_7)_2 Al_2 Cl_6$.

Phthalic chloride and butyric chloride seem to behave in a similar manner.

From these results, it would follow that in Friedel and Craft's method for the synthesis of the acetones, the acid chloride first combines with aluminium chloride, yielding the compound



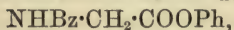
which is then acted on by the hydrocarbon or the phenol. The quantity of aluminium chloride necessary increases with the stability of this intermediate compound.

C. H. B.

Molecular Weight of Hydrogen Peroxide and of Benzoyl Peroxide. By W. R. ORNDORFF and J. WHITE (*Amer. Chem. J.*, 15, 347).—The authors have confirmed the result obtained by Carrara (this vol., ii, 163), that the molecular formula of hydrogen peroxide as determined by the freezing point method is H_2O_2 , and not H_4O_4 as found by Tammann (*Abstr.*, 1890, 106). The molecular weight of benzoyl peroxide calculated from the freezing point of its solutions in benzene and acetic acid, and from the boiling point of its solutions in ether and chloroform, was found to correspond with Brodie's formula, Bz_2O_2 .

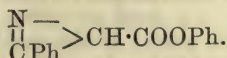
A. H.

Phenylic Hippurate and its Condensation Products. By F. WEISS (*Ber.*, 26, 1699—1702).—*Phenylic hippurate*,



is prepared by the action of phosphorus oxychloride (6—8 grams) on a mixture of hippuric acid (10 grams) and phenol (7 grams), and crystallises from alcohol in colourless plates melting at 104° . By the further action of phosphorus oxychloride on this compound, a condensation product, $C_{15}H_{11}NO_2$, is formed, crystallising from alcohol in long, colourless needles melting at 42° . The yield is 60—70 per cent. of the phenylic salt employed. The compound is volatile with steam and is not acted on by soda; it is readily hydrolysed by hydrochloric acid with the formation of phenol, hippuric acid, glycocine, and benzoic acid; its constitution is therefore probably

represented by the formula $NBz < \begin{smallmatrix} CH \\ || \\ C \end{smallmatrix} OP_h$, but it is at present impossible to decide definitely between this and the formula



J. B. T.

Condensation of Hippuric acid with Phthalic Anhydride and with Benzaldehyde. By E. ERLÉNMEYER, Jun. (*Annalen*, 275, 1—8).—When a mixture of hippuric acid and phthalic anhydride, in molecular proportion, is heated on the water-bath for half an hour with acetic anhydride (3 mols.), the *lactimide*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \\ \text{CO}\cdot\text{O} \end{smallmatrix} > \text{C}:\text{C} < \begin{smallmatrix} \text{N}\cdot\text{COPh} \\ \diagdown \\ \text{CO} \end{smallmatrix}$, is obtained; it crystallises from boiling nitrobenzene in canary-yellow needles, commences to darken at 240° , and decomposes at a high temperature.

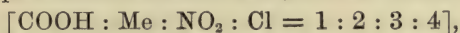
Benzoylamidocinnamic lactimide, $\text{CHPh}\cdot\text{C} \begin{smallmatrix} \diagup \\ \text{NCO}\cdot\text{Ph} \\ \diagdown \\ \text{CO} \end{smallmatrix}$, together with *sodium benzoylamidocinnamate*, is obtained in a similar manner from benzaldehyde, hippuric acid, sodium acetate, and acetic anhydride; it crystallises from benzene in long, yellowish needles, and melts at $165\text{--}166^\circ$. A. R. L.

Parachlororthotoluic acid and its Derivatives. By A. CLAUS and STAPELBERG (*Annalen*, 274, 285—304).—When 1 : 2-acetotoluidine is dissolved in glacial acetic acid and treated with bleaching powder solution, the *chloro-derivative* [$\text{NHAc} : \text{Me} : \text{Cl} = 1 : 2 : 4$] is obtained, together with a *dichloro-derivative* (see below). The *monochloro-derivative* forms colourless, silky needles, melts at 140° , and, when boiled with alcoholic potash for 8—10 hours, yields the *chlorotoluidine* [$\text{NH}_2 : \text{Me} : \text{Cl} = 1 : 2 : 4$]; this base boils at 246° , and melts at 16° (compare *Abstr.*, 1886, 1022). The corresponding *nitrile* obtained by the *diazo-reaction* (cuprous cyanide in the cold) forms yellowish needles, has a faint odour, melts at 67° , is sparingly soluble in hot water, and readily volatile with steam; *parachlororthotoluic acid*, formed by boiling the *nitrile* with alkalis, melts at 172° , and not at 130° , as stated by Krüger (*Abstr.*, 1885, 1053). The constitution of the acid is proved by the fact that it yields 1 : 2 : 4-chlorophthalic acid on oxidation. The *potassium salt* forms colourless needles with H_2O ; the *calcium salt* crystallises with $3\text{H}_2\text{O}$; the *barium salt* with $4\text{H}_2\text{O}$; the *amide* melts at 183° ; and the *ethylic salt* at 258° .

The *dichloroacetotoluidine* mentioned above [$\text{NHAc} : \text{Me} : \text{Cl}_2 = 1 : 2 : 4 : 6$] forms delicate needles or thin plates, melts at 186° , and yields the corresponding *derivative* of *orthotoluidine* when boiled with alcoholic potash; the latter is sparingly volatile with steam, forms colourless, lustrous needles, melts at 53° , and is converted into the *nitrile* melting at 92° by the *diazo-reaction*. When the *nitrile* is boiled with alcoholic potash, the *dichlorotoluic acid* is obtained; it crystallises in small, colourless needles, and melts at 181° .

When the *nitrate* of *chlorotoluidine* [$\text{NH}_2 : \text{Me} : \text{Cl} = 1 : 2 : 4$], which crystallises in bright red plates, and melts at 183° with decomposition, is added to cooled pure sulphuric acid (16—17 parts), the *nitro-derivative* [$\text{NH}_2 : \text{Me} : \text{Cl} : \text{NO}_2 = 1 : 2 : 4 : 5$] is obtained; it crystallises in yellow needles, and melts at 128° . When, however, the *nitrate* is added to 66 per cent. sulphuric acid (25 parts), and at the end of six hours the solution is poured on to ice, the last-mentioned *nitro-derivative* is precipitated, whilst if the mother liquor is then nearly neutralised, the *isomeride* [$\text{NH}_2 : \text{Me} : \text{Cl} : \text{NO}_2 = 1 : 2 : 4 : 6$] sepa-

rates; the latter crystallises in golden leaflets, and melts at 118—119°; the *acetyl* derivative is obtained by nitrating chloracetotoluidine dissolved in concentrated sulphuric acid with nitric acid (sp. gr. 1·45); it melts at 187°. *Nitrochlorotoluonitrile* $[\text{CN} : \text{Me} : \text{Cl} : \text{NO}_2 = 1 : 2 : 4 : 6]$ melts at 140°, and yields the corresponding *nitrochlorotoluic acid* melting at 189°. *Nitrochlorotoluonitrile* $[\text{CN} : \text{Me} : \text{Cl} : \text{NO}_2 = 1 : 2 : 4 : 5]$ melts at 86°, and the corresponding *nitrochlorotoluic acid* melts at 193°; the *potassium* salt crystallises with $\frac{1}{2}\text{H}_2\text{O}$, and the *magnesium* salt with $4\text{H}_2\text{O}$; the chlorine atom is displaced by the anilido-group when the acid is heated at 160—170° with aniline (compare Schöpf, Abstr., 1892, 535). The last-mentioned *nitrochlorotoluic acid* is the principal product of the action of nitric acid (sp. gr. 1·52) at 110—120° on *parachlororthotoluic acid*, but the isomeride



melting at 186°, is formed in smaller amount. The two acids are separated by means of their *magnesium* salts, that of the acid melting at 186° being the more soluble in water. The *nitro-acid* (m. p. 186°) is, however, obtained in good yield when *parachlororthotoluic acid* is heated at 100° with 10 parts of nitric acid of sp. gr. 1·52 and 30 parts of concentrated sulphuric acid; the *potassium* salt crystallises with $1\text{H}_2\text{O}$, and the *magnesium* salt crystallises with $5\text{H}_2\text{O}$.

When *parachlororthotoluic acid* is boiled with a mixture of nitric and sulphuric acids, or is heated with it in a sealed tube at 160°, the *dinitro-derivative* $[\text{COOH} : \text{Me} : (\text{NO}_2)_2 : \text{Cl} = 1 : 2 : 3 : 5 : 4]$, melting at 212°, is formed. A. R. L.

Iodoxy- and Iodoso-derivatives of Paratoluic acid. By E. KLOEPPPEL (*Ber.*, 26, 1733—1738; compare this vol., i, 506).—*Meta-iodoparatoluic acid*, $\text{C}_6\text{H}_3\text{MeI}\cdot\text{COOH}$ $[\text{Me} : \text{I} : \text{COOH} = 1 : 2 : 4]$, is obtained from the corresponding *amido-acid* by means of the *diazo-reaction*. It crystallises from ether in long, white needles, is readily soluble in alcohol, slightly in hot water, and melts at 205—206°. This acid does not yield an *iodoso-derivative*, either by v. Meyer's method (Abstr., 1892, 1460), or by that of Willgerodt (Abstr., 1893, i, 149). On boiling with fuming nitric acid, however, a *nitro-iodosoparatoluic acid* is formed as an amorphous powder, melting at about 160°. *Metaiodoparatoluic acid*, therefore, behaves in a similar manner to the *meta-* and *para-iodobenzoic acids* (this vol., i, 508).

Ortho-iodoparatoluic acid $[\text{Me} : \text{I} : \text{COOH} = 1 : 3 : 4]$ can also be prepared by means of the *diazo-reaction*, and forms white needles which melt at 127°. This acid behaves in a similar manner to *ortho-iodobenzoic acid* (this vol., i, 507), forming a *dichloride*, which on treatment with aqueous soda yields *iodosoparatoluic acid*; this separates from a large quantity of water in small crystals, which soften at 120°, and melt with decomposition at 167—169°. The *silver salt* does not explode on heating. A. H.

α -Benzoylamidophenylpropionic acid. By E. ERLÉNMEYER, Jun. (*Annalen*, 275, 13—20).— *α -Benzoylamidophenylpropionic acid*, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NHBz})\cdot\text{COOH}$, is prepared by reducing *benzoylamidocinnamic acid* with a slight excess of 2 per cent. sodium amalgam; it forms lustrous leaflets, melts at 182—183°, and is much more

stable towards alkalis than benzoylamidocinnamic acid. When heated with concentrated hydrochloric acid in a sealed tube at 150° for 15 hours, it yields phenylalanine and benzoic acid. A. R. L.

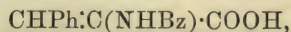
Separation of Cinnamic acid Dibromide into its Optically Active Components. By E. ERLIENMEYER, Jun. (*Ber.*, 26, 1659—1662).—The dibromide is separated by fractional precipitation with cinchonine, and by crystallisation of the cinchonine salts from alcohol. The dextrorotatory acid has been obtained with the rotation $[\alpha]_D = +48.15^{\circ}$. E. C. R.

Optically Active Cinnamic acid Dibromides. By C. LIEBERMANN (*Ber.*, 26, 1662—1663).—A question of priority.

Optically Active Cinnamic acid Dibromides. By C. LIEBERMANN and A. HARTMANN (*Ber.*, 26, 1664—1666).—The authors give an account of their attempt to quantitatively separate the optically active constituents. They have been only partially successful; but have proved that cinnamic acid dibromide contains only two optically active constituents.

The ethylic salt of dextro-rotatory cinnamic acid dibromide separates from carbon bisulphide in colourless crystals, melts at 71° , and has the rotation $[\alpha]_D = +59.1^{\circ}$. E. C. R.

Benzoylamidocinnamic acid. By E. ERLIENMEYER, Jun. (*Annalen*, 275, 8—13).—Benzoylamidocinnamic acid,



is obtained when the lactimide (last abstract) is suspended in water and heated with a slight excess of dilute sodium hydroxide, or with dilute sulphuric acid; the former reagent acts the more readily. It crystallises from alcohol in transparent prisms, and melts (according to its purity) between 210° and 228° , yielding the lactimide, phenylacetaldehyde, and carbonic anhydride; by energetic treatment with mineral acids or alkalis, it is decomposed with the formation of benzamide and phenylpyruvic acid, and on oxidation with potassium permanganate in alkaline solution it yields benzaldehyde. The ethylic salt is obtained by treating the lactimide with sulphuric acid and alcohol, or by adding sodium and a little alcohol to a mixture of ethylic hippurate and benzaldehyde suspended in ether; it forms delicate needles, and melts at 149° . A. R. L.

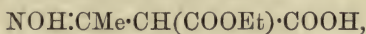
Abietic acid. By H. MACH (*Monatsh.*, 14, 186—201).—The various substances hitherto obtained from the resin of pine trees, and named respectively abietic, sylvic, and pimaric acids, are shown to be identical; the name *abietic acid* is retained. This acid occurs in colophonium in varying amount; some specimens of the resin contain 90 per cent. of the crude acid, from others no acid could be isolated. The method usually adopted was to digest the resin with 70 per cent. alcohol, and recrystallise the residual acid from methyl alcohol; or, in some cases, the crude acid was dissolved in 90 per cent. alcohol, precipitated with hydrochloric acid, and recrystallised from methyl

alcohol. Analyses and molecular weight determinations (cryoscopic and ebullioscopic) agree with the formula $C_{19}H_{28}O_2$. The acid forms white crystals, and melts at $153-154^\circ$ when slowly heated, beginning to soften at 148° . The *potassium salt*, $C_{19}H_{27}KO_2 \cdot 3C_{19}H_{28}O_2$, was prepared by neutralising an alcoholic solution of the acid with alcoholic potash, or boiling it with potassium carbonate; it forms bundles of silky needles, and melts at 183° . C. F. B.

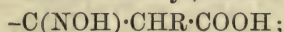
Formation of Inner Anhydrides from Ketoximic acids.

By A. HANTZSCH and A. MIOLATI (*Ber.*, **26**, 1689—1691).—*Ethylbenzoylacetic acid oxime*, $NOH:CPh \cdot CHEt \cdot COOH$, is prepared by the action of hydroxylamine on the ethereal salt in alkaline solution, and forms colourless crystals melting at $89-90^\circ$. It is not acted on by acetic anhydride or concentrated sulphuric acid.

Ethyl hydrogen acetylmalonate oxime,



is obtained from ethylic acetylmalonate and crystallises from dilute alcohol in small, colourless needles melting at 148° . The compound does not appear to form an anhydride, nor could it be hydrolysed; attempts to eliminate a carboxyl group were also unsuccessful. The authors point out the importance of both the position and nature of radicles in determining the formation of anhydrides from oximes; thus in the case of β -ethoximic acids, whilst hydrocarbon radicles directly linked to the $C:NOH$ group facilitate the formation of anhydrides, their action is precisely the reverse when they are linked to a carbon atom which is itself linked to carboxyl, as in the group

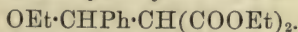


the same applies when $R = COOH$. This probably explains the failure of dimethylglyoxime, which is a "syn-" compound, to form an aldehyde.

J. B. T.

Addition of Sodium Alkylloxides. By C. LIEBERMANN (*Ber.*, **26**, 1876—1879).—The author has obtained direct additive compounds of sodium ethoxide and ethylic malonates of the general formula $>C:C(COOH)_2$.

Ethylic ethoxybenzylsodiummalonate, $OEt \cdot CHPh \cdot CNa(COOEt)_2$, is obtained by adding sodium ethoxide to an ethereal solution of ethylic benzalmalonate. It is a white powder which is decomposed by water into alkali and ethylic ethoxybenzylmalonate,



Methylic methoxybenzylsodiummalonate, ethylic ethoxyfurfurylsodiummalonate, ethylic ethoxypiperonylsodiummalonate, and methylic methoxypiperonylsodiummalonate have also been prepared.

These sodium compounds are only alkylated with difficulty, and on heating for a day with ethylic iodide at 100° the reaction had only partially taken place.

E. C. R.

Bromogallic acid and its Derivatives. By A. BIÉTRIX (*Bull. Soc. Chim.* [3], **9**, 241—243).—Bromogallic acid is difficult to separate from the dibromo-acid which is formed at the same time by the ordinary

method of preparation. The former is obtained together with unaltered gallic acid, from which it is readily separated by crystallisation, when less than the theoretical quantity of bromine dissolved in chloroform (3—4 parts) is gradually added to gallic acid. The pure acid, $C_6HBr(OH)_3 \cdot COOH + 3H_2O$, crystallises in small, hexagonal tables; the *acetyl* derivative melts at 95—96°. When barium hydroxide is added to a solution of the *ammonium* salt, a yellowish-orange coloration changing to green is produced; and on the addition of lead acetate to a solution of the *ammonium* salt, the *lead* salt separates as a white precipitate which later becomes green and finally dirty grey; the salt decomposes on fusion.

A. R. L.

Alkyltoluidinesulphonic acids. By R. SCHMIDT (*J. pr. Chem.* [2], 48, 46—69; compare Abstr., 1887, 1043—1044; 1891, 908; 1892, 334).—When potassium paratoluidinemetasulphonate is heated in a sealed tube with the calculated quantity of ethylic bromide and absolute alcohol at 150°, potassium sulphate and an oil are produced. The latter partially crystallises, and the portion which remains liquid is a mixture of ethyltoluidine and diethyltoluidine.

Diethyltoluidine hydrochloride melts at 157° and dissolves in alcohol, water, and warm benzene. *Ethyltoluidine hydrochloride* appears to be very unstable.

The crystalline *compound* forms colourless, monoclinic prisms (with $1H_2O$), melts at 243°, and is soluble in water and sparingly in absolute alcohol, but not in ether and benzene. Its molecular formula corresponds with that of diethyltoluidinesulphonic acid, but the *potassium salt*, $C_{11}H_{15}NSO_3K$, is the only salt which could be prepared; this crystallises in rhomboidal tables, melts at 297°, and dissolves in water.

Diethylparatoluidineorthosulphonic acid, $NEt_2 \cdot C_6H_3Me \cdot SO_3H + H_2O$, is obtained both by sulphonating diethyltoluidine and by heating potassium paratoluidineorthosulphonate with ethylic bromide in absolute alcohol; in the latter case, potassium sulphate is not a product of the reaction (compare above). The acid crystallises in beautiful, colourless prisms which are infusible, and are only sparingly soluble in water and in alcohol. The *potassium salt* crystallises in colourless, triclinic tables with $2H_2O$. The *barium salt*, with $4H_2O$, and the *calcium salt*, with $3H_2O$, were also crystallised.

The author discusses the possible constitution of the substance which melts at 243°, but does not arrive at any definite conclusion.

Ethylparatoluidineorthosulphonic acid, $NHEt \cdot C_6H_3Me \cdot SO_3H + H_2O$, is prepared by sulphonating ethyltoluidine; it crystallises in yellow prisms and is sparingly soluble in water and alcohol. The *potassium salt* crystallises in yellow tables with $1H_2O$, and is freely soluble in water. When the potassium salt is heated with ethylic bromide, it yields diethylparatoluidineorthosulphonic acid; the potassium salt of the latter acid remains unchanged when similarly treated.

By heating potassium paratoluidinemetasulphonate with isopropyl bromide, a *compound*, $C_{13}H_{21}NSO_3$, apparently containing two isopropyl groups, is obtained. It crystallises from water, and melts at 222—223°. When potassium paratoluidineorthosulphonate is similarly treated, an *isopropyltoluidinesulphonic acid* is obtained; it dis-

solves sparingly in water and very sparingly in alcohol, and crystallises in colourless prisms which do not melt at 300°.

A. G. B.

Action of some Alcohols on Paradiazotoluenemetasulphonic acid. By W. V. METCALF (*Amer. Chem. J.*, **15**, 301; compare Abstr., 1887, 136; 1888, 268; 1889, 975; this vol., i, 325).—This substance, like the corresponding orthodiao-compound, when boiled with alcohol under a *plus* pressure of 200 mm., yields a considerable proportion of ethoxytoluenesulphonic acid in addition to metatoluenesulphonic acid. The corresponding sulphonamides are difficult to separate, the mixture having been mistaken by v. Pechmann (*Annalen*, **169**, 47) for the pure metatoluenesulphonic acid.

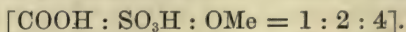
Parethoxytoluenemetasulphonamide, $\text{OEt}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_2\text{NH}_2$, forms white needles, slightly soluble in cold water; it melts at 138–139°. On oxidation with potassium permanganate, it yields *parethoxymetasulphonaminebenzoic acid*, which crystallises in long, white needles; it softens at 225° and melts at 230–231° with slight decomposition. The *barium salt* contains $2\text{H}_2\text{O}$. Methyl and propyl alcohol act in a similar manner to ethyl alcohol. Comparative experiments with methyl alcohol under *plus* pressures of 200, 400, and 600 mm. show that the proportion of methoxy-compound formed increases slightly with the pressure.

Paramethoxytoluenemetasulphonic chloride, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_2\text{Cl}$, crystallises from benzene in large, rhombic plates melting at 84°. The free *acid* forms yellowish needles melting at 92–95°, and yields crystalline barium, calcium, and lead salts. The *sulphonamide* crystallises in white needles, melts at 180–181°, and is only slightly soluble in boiling water. On oxidation, it yields *paramethoxymetasulphonaminebenzoic acid*, which forms white needles, and melts with decomposition between 240° and 270°; its *barium salt* contains $3\text{H}_2\text{O}$.

Parapropoxytoluenemetasulphonamide crystallises in needles, melts at 126.5–128°, and is nearly insoluble in cold water. A. H.

Action of Methyl Alcohol on Paradiazotolueneorthosulphonic acid. By R. M. PARKS (*Amer. Chem. J.*, **15**, 320; compare preceding abstract).—This compound, when heated with methyl alcohol, yields paramethoxytolueneorthosulphonic acid alone, the course of the reaction not being influenced by increase or diminution of the pressure. The product is identical with the oxymethyltoluenesulphonic acid of Limpricht and Heffter (*Annalen*, **221**, 344). The free acid is a dark brown liquid, which crystallises with great difficulty in rhombohedral plates; these decompose on heating without melting. The *barium salt* crystallises with $3\text{H}_2\text{O}$ and the *calcium salt* with $4\text{H}_2\text{O}$. The corresponding *sulphonic chloride* is a heavy, yellowish oil; the *sulphonamide* crystallises in white plates or prisms, is very soluble in alcohol, slightly so in water, and melts at 151°. On oxidation with potassium permanganate, the sulphonamide is partially converted into *paramethoxybenzoic sulphinide*, $\text{OMe}\cdot\text{C}_6\text{H}_3\cdot\begin{smallmatrix} \text{SO}_2 \\ \text{CO} \end{smallmatrix}\text{NH}$, which forms long, slender needles, melts at 271°, and is easily soluble in boiling alcohol. The acid potassium salt of *paramethoxyorthosulphobenzoic*

acid is also formed in this reaction, and by the oxidation of potassium paramethoxytolueneorthosulphonate; it crystallises in long prisms containing $1\text{H}_2\text{O}$. The chloride of the sulphobenzoic acid, $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{SO}_2\text{Cl})\cdot\text{COCl}$, forms small, colourless crystals, and on boiling with water yields the free acid; this substance dissolves readily in water, crystallises in long needles, and melts without decomposition at 104° . This acid yields resorcinol and 1 : 2 : 4-dihydroxybenzoic acid on fusion with potash, so that its constitution is



The isomeric acid obtained by Zervas (*Annalen*, 103, 338) by the direct sulphonation of anisic acid is therefore the 1 : 3 : 4-compound.

A. H.

Monochloro-derivatives of Ortho-xylene, and their Relation to the Chlororthotoluic acids. By A. CLAUS and R. BAYER (*Annalen*, 274, 304—311).—It having been shown that the melting point of parachlororthotoluic acid is incorrectly given by Krüger (*Abstr.*, 1885, 1053), the authors have repeated the whole of this chemist's experiments.

A mixture of about 2 parts of 4-chlorortho-xylene and 1 part of 3-chlorortho-xylene is obtained by chlorinating orthoxylenes in presence of iron.

4-Chlorortho-xylene-5-sulphonic acid forms colourless needles or nacreous plates containing $5\text{H}_2\text{O}$; 3-chlorortho-xylene-6-sulphonic acid is more sparingly soluble in water than the isomeride, and crystallises in small, prismatic needles with $2\text{H}_2\text{O}$. The two chlorortho-xylenes, obtained by the hydrolysis of the sulphonic acids, agree with Krüger's description; they were oxidised by heating with nitric acid at 160° , and the chlororthotoluic acids converted into their calcium salts. The more sparingly soluble calcium salt, with $2\text{H}_2\text{O}$, is, in accordance with Krüger's statement, derived from the acid $[\text{COOH} : \text{Me} : \text{Cl} = 1 : 2 : 5]$, but this acid melts at 137° (not 166°); the calcium salt of the acid $[\text{COOH} : \text{Me} : \text{Cl} = 1 : 2 : 4]$ crystallises with $3\text{H}_2\text{O}$, and the acid melts at 170° (not 130°).

The acid melting at 156° $[\text{COOH} : \text{Me} : \text{Cl} = 1 : 2 : 3]$ is obtained by oxidising 1 : 2 : 3-chlorortho-xylene, as stated by Krüger. The two meta-acids, melting at 137° and 156° respectively, are obtained (the former predominating) by passing chlorine into a solution of orthotoluic acid in glacial acetic acid.

A. R. L.

α -Hydrindone and its Derivatives. By A. KÖNIG (*Annalen*, 275, 341—351; compare Gabriel and Hausmann (*Abstr.*, 1889, 1172)).—Hydrocinnamorthocarboxylic acid was prepared, as already described (*Abstr.*, 1888, 150). When either the acid or its calcium salt, preferably the former, is distilled, α -hydrindone is formed; it melts at $40\text{--}41^\circ$, boils at $241\text{--}242^\circ$ (739 mm.), has a sp. gr. at $42^\circ = 1.099$, and yields phthalic acid on oxidation with nitric acid. The oxime melts at $144\text{--}144.5^\circ$, and the hydrazone melts at $130\text{--}131^\circ$. When α -hydrindone is dissolved in glacial acetic acid (10 parts), and chlorine passed through the boiling solution, a dichloro-derivative, $\text{C}_9\text{H}_6\text{Cl}_2\text{O}$, is obtained, which crystallises in thick needles,

and melts at 74—74.5°; whilst when a boiling solution of α -hydrindone in an equal weight of glacial acetic acid is treated with chlorine, tetrachlorhydrindone (Zincke and Frölich, *Abstr.*, 1887, 955) is formed; it melts at 104.5—105.5°.

α -Amidohydrindene, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{---} \end{smallmatrix} > \text{CH} \cdot \text{NH}_2$, is obtained when α -hydrindoneoxime is reduced in alcoholic solution with sodium amalgam, keeping the liquid faintly acid with acetic acid meanwhile; it is a colourless oil having a faint, aniline-like odour, and boils at 220.5° under a pressure of 747 mm. The *hydrochloride* crystallises in colourless needles, and melts at 208°, and the *sulphate* forms plates, and melts at 256—257°.

α -Hydroxyhydrindene, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{---} \end{smallmatrix} > \text{CH} \cdot \text{OH}$, is not formed by reducing α -hydrindone with sodium amalgam, but it is produced when an aqueous solution of α -amidohydrindene hydrochloride is heated on the water-bath with sodium nitrite; it forms small crystals having the odour of naphthalene, and melts at 54—54.5°. It boils at 220° with partial decomposition into a hydrocarbon, which can also be obtained by heating the hydroxy-compound with zinc chloride; analysis of the hydrocarbon gave values agreeing better with those required for hydrindene than for indene.

A. R. L.

β -Hydrindone and its Derivatives. By H. BENEDIKT (*Annalen*, 275, 351—356).— β -Hydrindone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{---} \end{smallmatrix} < \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{---} \end{smallmatrix} > \text{CO}$, is obtained by distilling dehydrated calcium orthophenylenediacetate; it crystallises in colourless, flat needles, has the odour of jasmine, melts at 61°, is volatile with steam, boils with partial decomposition at 220—225°, and is converted into a brown, viscid mass on exposure to the air. Wislicenus has already published a preliminary account of this compound (*Tageblatte d. Naturforsch.-Versamm.*, 1889), and he, therefore, claims the priority of its discovery over Schad (this vol., i, 280).

When β -hydrindone is oxidised with warm nitric acid, it yields phthalic acid, but is converted into homophthalic acid (W. Wislicenus, *Abstr.*, 1886, 879) when an ethereal solution is shaken with an aqueous solution of potassium permanganate. The *oxime*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{---} \end{smallmatrix} < \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{---} \end{smallmatrix} > \text{C} \cdot \text{NOH}$, melts at 155°, and when treated with sodium amalgam in glacial acetic acid solution, yields a small quantity of the amido-base.

A. R. L.

Synthesis of α -Phenylindoxazen from Orthamidobenzophenoneoxime. By F. v. MEYENBURG (*Ber.*, 26, 1657—1658).—Phenylindoxazen, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CPh} \\ | \\ \text{---} \end{smallmatrix} > \text{N}$, is obtained by adding sodium nitrite to a solution of orthamidobenzophenoneoxime in excess of very dilute hydrochloric acid, and after quickly filtering the mixture, heating it over a bare flame. It crystallises well, and melts at 83—84°. Only the pure high melting modification of orthamidobenzophenoneoxime is convertible into phenylindoxazone.

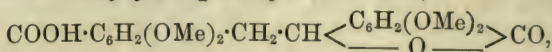
E. C. R.

Orthodiamidodiphenyl. By E. TÄUBER (*Ber.*, **26**, 1703—1705; compare Abstr., 1891, 570).—Carbazole is obtained by heating ortho-tetrazodiphenyl with potassium hydrosulphide on the water-bath in aqueous solution, but the author is at present unable to explain its formation.

It has been previously shown (this vol., i, 96) that orthodiamidodiphenyl combines with benzile, and that the compound which is formed yields a reduction product $\begin{matrix} \text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CHPh} \\ \text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CHPh} \end{matrix}$; the dinitroso-derivative has now been analysed. The *diacetyl derivative* is deposited from acetic acid in granular crystals melting at 280°. The above reduction compound is not acted on by heating with 20 per cent. hydrochloric acid.

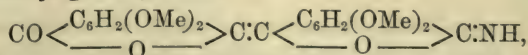
Diamidoditolyl, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2$ [$\text{C}_6\text{H}_3 : \text{NH}_2 : \text{Me} = 1 : 2 : 5$], reacts with benzile in a similar manner to diamidodiphenyl; the yellow condensation product melts at 235°, and on reduction yields a colourless, basic compound melting at 163°. J. B. T.

Tetramethoxydiphthalyl. By R. LÖWY (*Monatsh.*, **14**, 131—145).—Tetramethoxydiphthalyl (compare Goldschmidt and Egger, Abstr., 1891, 1371), when warmed with alcoholic potash in an atmosphere of hydrogen, is converted into *tetramethoxydiphthalyl-lactonic acid*, $\text{COOH}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{C}(\text{OH})\cdot\text{C} < \begin{smallmatrix} \text{C}_6\text{H}_2(\text{OMe})_2 \\ \text{O} \end{smallmatrix} > \text{CO}$, and a little tetramethoxydiphthalylldicarboxylic acid. The former acid was obtained in yellow crystals, which melt with decomposition at 284—292°; the *copper salt*, $\text{C}_{40}\text{H}_{34}\text{O}_{18}\text{Cu}$, as a greenish-blue precipitate. When tetramethoxydiphthalyl is reduced with zinc and potash, it yields *tetramethoxyhydrodiphthalyl-lactonic acid*,



which forms white crystals, melting at 186—187°. When boiled with hydriodic acid and phosphorus, tetramethoxydiphthalyl yields *tetrahydroxydibenzylldicarboxylic acid*, $\text{C}_2\text{H}_4[\text{C}_6\text{H}_2(\text{OH})_2\cdot\text{COOH}]_2$, as a yellow, crystalline substance, which turns greenish by oxidation on exposure to air, and melts above 300°; the *barium salt*, $\text{C}_{16}\text{H}_{12}\text{O}_8\text{Ba} + \text{H}_2\text{O}$, forms greenish-yellow crystals. Tetramethoxydiphthalyl takes up two atoms of bromine when boiled with the latter in chloroform solution, yielding *tetramethoxydiphthalyl dibromide*, which crystallises in lemon-yellow, silky needles, and begins to decompose at 100°.

Tetramethoxydiphthalylimide,



is obtained when tetramethoxydiphthalyl-lactonic acid is heated in a sealed tube with strong ammonia at 100°; it is a yellow substance, which turns brown at about 200°, but is not melted at 310°. The substances described in this paper all exhibit colour reactions with sulphuric acid, &c. In general, the behaviour and derivatives of tetramethoxydiphthalyl are analogous to those of diphthalyl itself.

C. F. B.

Preparation of Triphenylacetoneitrile and Triphenylcarbinol. By L. BOUVEAULT (*Bull. Soc. Chim.* [3], 9, 373—375).—Triphenylcarbinol is most easily prepared by decomposing triphenylbromomethane with a solution of sodium carbonate, which, by neutralising the hydrobromic acid as fast as it is formed, greatly accelerates the action of the water (compare Hémilian, this Journal, 1875, 152).

Triphenylacetoneitrile is best prepared by treating triphenylbromomethane with mercuric cyanide in the same manner as that adopted by E. and O. Fischer for the treatment of triphenylchloromethane (*Abstr.*, 1879, 326). The product of the reaction is extracted with boiling benzene, and the solution is filtered and distilled; the residue, consisting of the nitrile, is recrystallised from ether.

A. G. B.

Action of Hydroxylamine on Orthobenzoylbenzoic acid.

By F. H. THORP (*Ber.*, 26, 1795—1796; compare this vol., i, 466).

—The compound recently described by the author as the oxime of benzoylbenzoic acid is in reality its *anhydride*, which has already been prepared by Hantzsch and Miolati (this vol., ii, 574); the salts of the corresponding acid are readily obtained by dissolving the anhydride in alkali, and adding metallic salts; the *silver ammonium* salt, $\text{NOAg} \cdot \text{CPh} \cdot \text{COONH}_4$, is a white precipitate, which becomes crystalline after a time, and darkens in the light. The *barium* salt, $\text{C}_{14}\text{H}_9\text{O}_3\text{NBa}$, is also a crystalline precipitate, and the *potassium* salt, $\text{C}_{14}\text{H}_9\text{O}_3\text{NK}_2 + 3\text{H}_2\text{O}$, forms thin, transparent plates, which are very soluble in water.

H. G. C.

Condensation of Deoxybenzoïn with Aldehydes and Ketones.

By F. KLINGEMANN (*Annalen*, 275, 50—83).—*Benzamarone* melts at 217—218°, and determinations of its molecular weight by the cryoscopic method show that it has not the formula $\text{C}_{70}\text{H}_{56}\text{O}_4$, assigned to it by Zinin, but the formula $\text{C}_{35}\text{H}_{28}\text{O}_2$; it is, therefore, formed from benzaldehyde (1 mol.) and deoxybenzoïn (2 mols.), with the elimination of 1 mol. H_2O (compare *Abstr.*, 1889, 265).

Metanitrobenzamarone, $\text{NO}_2 \cdot \text{C}_{35}\text{H}_{27}\text{O}_2$, is formed in a similar manner from metanitrobenzaldehyde and deoxybenzoïn; it crystallises in delicate, yellowish needles, and melts at 220°. Ethyldeoxybenzoïn does not yield a condensation derivative with benzaldehyde; hence the CH_2 group in deoxybenzoïn takes part in the reaction.

The two isomerides, $\text{C}_{21}\text{H}_{16}\text{O}$, obtained by distilling benzamarone (this vol., i, 353), crystallise in the monoclinic system; the crystals of the modification melting at 101—102° have axial relations $a : b : c = 3.2899 : 1 : 2.3846$; $\beta = 87^\circ 8'$; whilst the crystals of that melting at 89—90° have axial relations

$$a : b : c = 0.8389 : 1 : 1.5537; \beta = 56^\circ 26'.$$

Both the isomerides are converted into sodium amarate when boiled with sodium ethoxide, but no such reaction occurs when sodium methoxide is used; indeed Zinin's observation that a lower homologue of amaric acid is formed when benzamarone is heated with sodium methoxide appears to be erroneous. In the preparation of

amaric anhydride from benzamarone, it is preferable to employ sodium ethoxide instead of a solution of sodium hydroxide in alcohol, as recommended by Zinin.

Dimethylamaric acid, $C_{23}H_{26}O_3$, is obtained by cohobating benzamarone with sodium isobutoxide; it forms monoclinic crystals, $a : b : c = 2.9249 : 1 : 2.5452$; $\beta = 82^\circ 57' 10''$, and melts at 182° .

When amaric anhydride is heated at 100° with alcoholic ammonia, and the product is precipitated from water, a mixture of *amaric amide*, $C_{23}H_{33}NO_2$, which crystallises in white needles, and melts at $145\text{--}152^\circ$, and an *amide*, $C_{23}H_{25}NO_3$, which forms small, flat crystals, and melts at 124° , is obtained; whilst on adding hydrochloric acid to the filtrate, the monobasic acid, $C_{23}H_{24}O_4$, from which the second amide is derived, separates; it forms small transparent prisms, melts at $127\text{--}135^\circ$, and yields amaric anhydride when heated; the *silver salt* is a flocculent precipitate fairly stable towards light.

When amaric anhydride is dissolved in glacial acetic acid, and nitric acid added, or when it is treated with alcoholic sulphuric acid, a *compound*, $C_{21}H_{18}O_2$, melting at $163\text{--}168^\circ$, is formed; on hydrolysis with alcoholic potash, it yields a soluble salt.

When amaric acid is oxidised with chromic acid or alkaline potassium permanganate, α - and β -*dehydroamaric acid*, $C_{23}H_{20}O_3$, are formed. The α -acid melts at 173° , resolidifies at a higher temperature, and then melts at 238° , which is the melting point of the β -acid, into which it is converted. The *anhydride*, $C_{23}H_{18}O_2$, is obtained by distilling the β -acid under diminished pressure; it melts at $129\text{--}130^\circ$, and when heated with alcoholic ammonia at 100° , yields a very stable amide, $C_{23}H_{21}NO_2$, melting at 232° . The β -acid is regenerated when the amide is treated with alcoholic potash. When β -dehydroamaric acid is fused with potash, it yields benzoic acid and pyroamaric acid, $C_{16}H_{16}O_2$, melting at $95\text{--}96^\circ$.

The compound $C_{36}H_{28}O_2$, melting at 198° , is obtained by the condensation of deoxybenzoïn with acetophenone, and the *compound* $C_{33}H_{26}O_3$ is obtained by the condensation of deoxybenzoïn with furfuraldehyde.

A. R. L.

Diphenylacetic Acid. By F. KLINGEMANN (*Annalen*, 275, 83—89).—*Diphenylacetanilide*, $C_{20}H_{17}NO$, is prepared by treating an ethereal solution of diphenylacetic chloride with aniline; it forms colourless needles, and melts at 180° ; the *hydrazide*, $C_{20}H_{18}N_2O$, melts at 168° ; the *amide* is obtained by passing dry ammonia into an ethereal solution of the chloride; it is converted into the *nitrile* by means of phosphorus pentachloride. On ethylation, this *nitrile* yields *ethyl-diphenylacetoneitrile*, boiling at 183° (13 mm.); it is scarcely attacked when boiled with alcoholic potash, but on being heated in a sealed tube at 210° with a mixture of glacial acetic and hydrochloric acids it yields *ethyldiphenylacetic acid*, which forms transparent crystals, and melts at $173\text{--}174^\circ$. It is, therefore, not identical with pyroamaric acid (last abstract).

When diphenylacetic chloride is treated with benzene and aluminium, triphenylmethane is obtained together with small quantities of phenyldeoxybenzoïn, which crystallises in small, white

needles, and melts at 125—128°, and a hydrocarbon, $C_{38}H_{30}$, forming yellow crystals and melting at 168°. A. R. L.

Dihydronaphthalene and some of its Derivatives. By E. BAMBERGER and W. LODTER (*Ber.*, 26, 1833—1844; compare *Abstr.*, 1891, 1072).—The additional hydrogen atoms in dihydronaphthalene occupy the para- or 1:4-position, and not the ortho- or 1:2-position as was formerly supposed. This is proved by the fact that, on oxidation, it yields orthophenylenediacetic acid, $C_6H_4(CH_2\cdot COOH)_2$. The hydrocarbon is closely analogous to ethylene, and, like the latter, forms a *dibromide*, which is reconverted by the action of alcohol and zinc-dust into dihydronaphthalene, and, on treatment with potassium carbonate, yields *tetrahydronaphthalene glycol*, $C_{10}H_{10}(OH)_2$; this crystallises in silver-white plates, resembling naphthalene in appearance, melts at 135°, and is not volatile with steam. It dissolves to a moderate extent in cold water, and readily in hot water, alcohol, and chloroform. It has all the properties of a glycol, being insoluble in alkalis, and unacted on by diazo-compounds. The *benzoate* melts at 89—90°, the *acetate* at 109·5—110°, and the *bisphenylurethane* at 148—150°: all these derivatives being crystalline. On oxidation, it yields orthophenylenediacetic acid, together with a smaller amount of orthocarboxyphenylacetic acid, $COOH\cdot C_6H_4\cdot CH_2\cdot COOH$, and other products. On treatment with hydrogen chloride, it is converted into tetrahydronaphthalene chlorhydrin, $C_{10}H_{10}Cl\cdot OH$, which forms long, silky needles melting at 117·5°; this sublimes readily at 100°, and is slightly soluble in cold water, readily in alcohol, &c. The chlorhydrin is best prepared by treating dihydronaphthalene itself with hypochlorous acid. The *acetate* forms groups of prisms which melt at 47°, and deliquesce in ether or chloroform vapour; the *benzoate* crystallises in needles melting at 64—65°.

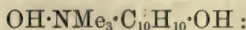
The action of alkalis on the chlorhydrin is of a complicated nature, the products of the reaction varying with the conditions of the experiment. The most readily formed of these products is *tetrahydronaphthylene oxide*, $C_6H_4<\begin{smallmatrix} CH_2\cdot CH \\ | \\ CH_2\cdot CH \end{smallmatrix}>O$, which is very similar in chemical properties to ethylene oxide, of which it is the closed chain analogue. This substance is dimorphous, crystallising in thick plates, which belong either to the monosymmetric or asymmetric system, according to the circumstances of crystallisation. It melts at 43·5°, volatilises with extreme readiness with steam, and distils without decomposition at 257—259° under a pressure of 715 mm. It is tolerably soluble in hot water, readily in organic solvents. Like ethylene oxide, it does not react with hydroxylamine or phenylhydrazine. It readily unites with hydrogen chloride and hydrogen bromide to form the corresponding hydrins, and even precipitates ferric hydrate from solutions of ferric chloride. It also combines, although less readily, with water, producing the glycol, and very readily with organic bases to form alkines, which closely resemble the hydroxylamines of Wurtz. Of these, the following have been prepared by the direct action of the base on the chlorhydrin:—

Dimethyltetrahydronaphthylalkine, $\text{NMe}_2 \cdot \text{C}_{10}\text{H}_{10} \cdot \text{OH}$, an alkaline oil which boils at 183° (27 mm.).

Diethyltetrahydronaphthylalkine, $\text{NEt}_2 \cdot \text{C}_{10}\text{H}_{10} \cdot \text{OH}$, boiling at 202° (38 mm.).

Piperidyltetrahydronaphthylalkine, $\text{C}_5\text{NH}_{10} \cdot \text{C}_{10}\text{H}_{10} \cdot \text{OH}$, crystallises in colourless needles melting at $46\text{--}48^\circ$.

Trimethylhydroxytetrahydronaphthylammonium hydroxide,



a syrup which crystallises with difficulty, and acts as an alkali. The chloride forms lustrous, monosymmetric prisms melting at 243° . This compound is the closed chain analogue of choline, which it resembles in all its properties.

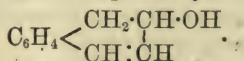
Dihydroxytetrahydronaphthylethylenediamine, $\text{C}_2\text{H}_4(\text{NH} \cdot \text{C}_{10}\text{H}_{10} \cdot \text{OH})_2$, forms groups of white needles, melts at 201° , and is soluble in alcohol, benzene, &c., scarcely soluble in water. Diacid base.

Hydroxytetrahydronaphthylamine, $\text{NH}_2 \cdot \text{C}_{10}\text{H}_{10} \cdot \text{OH}$, which is an alkaline oil; the hydrochloride forms needles melting at 265° ; the phthalimide compound is a colourless, crystalline powder melting at $217\text{--}218.5^\circ$.

Dihydroxytetrahydronaphthylamine, $\text{NH}(\text{C}_{10}\text{H}_{10} \cdot \text{OH})_2$, forms long, refractive prisms, melts at $165\text{--}166^\circ$, and is almost insoluble in water, but soluble in alcohol, &c.

A series of *alkeines* has also been prepared, but are not described in detail.

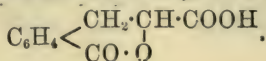
When the chlorhydrin is submitted to the continued action of an alkali, the tetrahydronaphthylene glycol becomes converted into the isomeric *dihydronaphthol*, which probably has the formula



This substance is an unsaturated alicyclic alcohol, is insoluble in alkalis, &c., and readily combines with bromine. It is obtained as an oil boiling at $162\text{--}168^\circ$ (28 mm.), but has probably not yet been prepared quite pure. Mineral acids at once convert it into naphthalene, and its presence can readily be recognised. The reaction with bromine is not of the nature of a simple addition, the only product which has been isolated having the composition of a brominated tetrahydronaphthyleneglycol, $\text{C}_{10}\text{H}_8\text{Br}(\text{OH})_2$.

Dihydronaphthol is also capable, when acted on by an alcohol, of uniting with the elements of water to form *tetrahydronaphthylenemeta-glycol*, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_2 \text{---} \text{CH} \cdot \text{OH} \\ | \\ \text{CH}(\text{OH}) \cdot \text{CH}_2 \end{array} .$ This compound is obtained as an oil boiling at $175\text{--}178^\circ$ (20 mm.), but solidifies, on standing, to white needles melting at 49° , and can be recrystallised from light petroleum. It is insoluble in alkalis, and is not decomposed by mineral acids.

On oxidation with potassium permanganate, dihydronaphthol is converted into *dihydroisocoumarincarboxylic acid*,



a substance which is also formed by the action of sodium amalgam on isocoumarincarboxylic acid. This forms fascicular groups of lustrous needles, melts at 153.5° , and is readily soluble in hot water, alcohol, and boiling chloroform. It is a lactonic acid, and neutralises one equivalent of an alkali in the cold, two on heating. It is reduced by phosphorus and hydriodic acid to orthocarboxyhydrocinnamic acid. Tetrahydronaphthylene chlorhydrin is converted by the action of dilute alkalis into *monoketotetrahydronaphthalene*, $C_6H_4 < \begin{smallmatrix} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CO \end{smallmatrix}$. This substance has a pleasant ketone-like

odour, and combines with sodium hydrogen sulphite and phenylhydrazine to form crystalline products. Finally, hot concentrated alkaline solutions convert the chlorhydrin into naphthalene.

A more detailed account of these researches is to be published later on in the *Annalen*.
A. H.

Oxidation of Naphthalic acid. By C. GRAEBE and F. BOSSEL (*Ber.*, 26, 1797—1799).—When naphthalic acid is oxidised by alkaline potassium permanganate, it is converted into *dicarboxyphenylglyoxylic acid*, $COOH \cdot CO \cdot C_6H_3(COOH)_2$, [$(COOH)_2 : CO = 1 : 3 : 2$], which is a crystalline compound melting at 238° (corr.) with decomposition. During the oxidation, a portion of the acid loses carbonic anhydride, forming the carboxyorthophenylglyoxylic acid already prepared by Zincke and Breuer. The dicarboxy-acid combines with phenylhydrazine to form a *hydrazone*, and, on reduction with phosphorus and hydriodic acid, yields 1:2:6-*toluenedicarboxylic acid*, $C_6H_3Me(COOH)_2$, which melts without decomposition at 235° , and is oxidised by alkaline permanganate to hemimellitic acid, $C_6H_3(COOH)_3$.

When dicarboxyphenylglyoxylic acid is heated at 240 — 260° , water, carbonic anhydride, and carbonic oxide are evolved; the residue contains, in addition to hemimellitic acid, two substances, one of which may be extracted by boiling water, and consists of *benzaldehydedicarboxylic acid*, $CHO \cdot C_6H_3(COOH)_2$; it forms colourless crystals, is readily soluble in water, melts at 175 — 178° , and combines with phenylhydrazine to form a *hydrazone*. The second compound is insoluble in water, has the composition $C_9H_4O_4$, and does not melt at 340° ; on warming with phenylhydrazine and alcohol, it yields the *hydrazone* obtained from benzaldehydedicarboxylic acid, and is, therefore, probably the *dilactone* of this acid, $C_6H_3 < \begin{smallmatrix} COO \\ | \\ COO \end{smallmatrix} CH$.

Nitronaphthalic acid, on oxidation with alkaline permanganate, yields dicarboxynitrophenylglyoxylic acid.
H. G. C.

Chrysene. By E. BAMBERGER and F. CHATTAWAY (*Ber.*, 26, 1745—1751).—Chrysenic acid, $C_{17}H_{12}O_2$ (*Abstr.*, 1890, 1312), on distillation with lime under diminished pressure (40—50 mm.), yields a mixture of chrysoketone and a hydrocarbon which is identical with β -phenylnaphthalene (this vol., i, 522). The hydrocarbon obtained by Graebe (*Ber.*, 6, 66; 7, 782) by the distillation of chrysoquinone with soda-lime, is also identical with this product. Chrysene is

therefore a derivative of this hydrocarbon, and has the formula $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{CH} \\ | \\ \text{C}_{10}\text{H}_6 \cdot \text{CH} \end{array}$, chrysenic acid being probably β -phenylnaphthoic acid, $\text{C}_{10}\text{H}_6\text{Ph} \cdot \text{COOH}$ (compare next abstract). The $\text{CH}=\text{CH}$ group of the hydrocarbon and the carboxyl of the acid are probably combined with the α -carbon atom of the naphthalene ring. A. H.

Picene. By E. BAMBERGER and F. CHATTAWAY (*Ber.*, **26**, 1751—1754).—Picene melts at 350° (uncorr.), 364° (corr.), and has, therefore, a higher melting point than any other known hydrocarbon. It yields a quinone, $\text{C}_{20}\text{H}_{14}(\text{CO})_2$, which behaves as an ortho-diketone, and an acid, $\text{C}_{21}\text{H}_{14}\text{O}_2$, which closely resembles chrysenic acid, and has, therefore, been named picenic acid. As this substance, on distillation with lime, yields $\beta\beta$ -dinaphthyl, it follows that picenic acid is β -naphthylnaphthoic acid, $\text{C}_{10}\text{H}_7 \cdot \text{C}_{10}\text{H}_6 \cdot \text{COOH}$, whilst picene itself is $\beta\beta$ -dinaphthylethylene, $\begin{array}{c} \text{C}_{10}\text{H}_6 \cdot \text{CH} \\ || \\ \text{C}_{10}\text{H}_6 \cdot \text{CH} \end{array}$.

Picene is therefore the phenanthrene of the naphthalene series, and is closely related to chrysene (compare preceding abstract). Picene also furnishes a ketone, $(\text{C}_{10}\text{H}_6)_2\text{CO}$, obtained by distilling picenequinone with lead oxide; this corresponds with diphenylene ketone and chrysoketone, and, on reduction, gives rise to picene-fluorene alcohol, $\text{CH}(\text{C}_{10}\text{H}_6)_2\text{OH}$, and picene-fluorene, $\text{CH}_2(\text{C}_{10}\text{H}_6)_2$. The three hydrocarbons, picene, chrysene, and phenanthrene, therefore, resemble one another very closely, and may be converted by similar steps into their parent hydrocarbons, $\beta\beta$ -dinaphthyl, β -phenylnaphthalene, and diphenyl. A. H.

American Oil of Turpentine. By J. H. LONG (*J. Anal. Chem.*, **7**, 99—108).—The specific gravity and specific rotation of nearly 40 samples of oil of turpentine have been determined, including commercial products and specimens prepared in the manner described by the author, so as to exclude changes brought about by exposure to air or during distillation. It appears from these results that the oil collected from spruce trees is laevorotatory, $[\alpha]_D = -34.828$; in two cases the rotation was greater than that observed by Tilden for pure australene, namely, $+29.581$ and $+25.114$ respectively. Exposure of the gum on the trees does not appear to lower the rotatory power of the product. Pinene is accompanied in the turpentine by a laevorotatory compound of higher boiling point, and the author suggests that this may possibly be the hitherto unknown laevorotatory cymene. On exposure to light during 20 days, commercial turpentine exhibits a slight increase in rotation; but no precautions were taken to exclude moisture, or even air. By the action of air, the specific rotation, specific gravity, and boiling point rise, and the turpentine becomes yellow. The compound formed by the action of sodium on commercial turpentine appears to be without effect on the rotatory power, since the latter is practically unchanged after the removal of the sodium compound. The rotatory power of the hydrochloride, $\text{C}_{10}\text{H}_{16}\text{HCl}$, was also determined, $= +7.036$, that of the original

turpentine being +15.607, although the absence or otherwise of the lævopinene derivative was not proved; the results appear to show that the relationship in molecular rotatory power between compounds and their simple derivatives is fallacious (compare Flawitzky, *Ber.*, **15**, 5).

J. B. T.

Terpineol. By O. WALLACH and F. KERKHOFF (*Annalen*, **275**, 103—110).—Bouchardat and Voiry (*Abstr.*, 1887, 677) obtained terpineol in a solid crystalline form; the authors find that it melts at 35° and remains in superfusion for long periods. The terpenyl-phenylurethane, which it yields by combination with phenylcarbimide, melts at 113°. When terpineol is heated at 180—190° with potassium hydrogen sulphate, dipentene is the chief product; boiled with dilute sulphuric acid for an hour, it yields terpinene, cineole, terpinolene, and traces of dipentene; whilst if heated on the water-bath for seven hours with glacial acetic acid and a little dilute sulphuric acid, a small portion is converted into cymene and a little terpinene. When terpineol is boiled with 20 per cent. phosphoric acid, terpinene, cineole, and a small quantity of a hydrocarbon, yielding a solid bromide, are obtained. By boiling terpineol with a 50 per cent. solution of oxalic acid for five hours, the product consists mainly of terpinene, but small quantities of cineole and of terpinolene are also produced; when the boiling is of shorter duration, more terpinolene is obtained.

Experiments show that the bromine atoms are more readily removed from terpinolene tetrabromide when it is boiled with alcoholic potash than from the tetrabromides of limonene and dipentene.

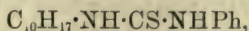
A. R. L.

Dihydrocarveol. By O. WALLACH, H. KRUSE, and F. KERKHOFF (*Annalen*, **275**, 110—133).—Dihydrocarveol (*Abstr.*, 1892, 499) is obtained by reducing either dextro- or lævo-carveol with sodium and alcohol; it rotates the plane of polarised light in the same direction as the carveol from which it is obtained. It has an odour recalling that of terpineol, boils at 224—225° under the ordinary pressure, and at 112° under 14 mm. pressure; it has a sp. gr. at 20° = 0.927, and a refractive power $[n]_D = 1.48168$. The phenylurethane, $C_{10}H_7O \cdot CONHPh$, obtained from both optical antipodes, melts at 87°, whilst the inactive (*racemic*) modification melts at 93°. Dihydrocarveol is an unsaturated compound, and exhibits great similitude to terpineol. When dihydrocarveol is boiled with dilute sulphuric acid, terpinene is formed.

Dihydrocarvone, $C_{10}H_{16}O$, obtained by boiling a solution of dihydrocarveol in glacial acetic acid with an aqueous solution of chromic acid, can be purified by means of its compound with sodium hydrogen sulphite. It boils at 221—222°, and its vapour has the odour of menthone, or of carveol; its sp. gr. at 19° is 0.928, its specific refractive power $[n]_D = 1.47174$. It is dextro- or lævo-rotatory according as it originates from dextro- or lævo-dihydrocarveol. The optically active *oximes*, $C_{10}H_{16} \cdot NOH$, melt at 88—89°, whilst the inactive (*racemic*) modification melts at 115—116°.

Dihydrocarvylamine, $C_{10}H_{17} \cdot NH_2$, is the compound described by Goldschmidt (*Abstr.*, 1887, 249 and 475) as carvylamine, and is best prepared by reducing carvoxime with sodium and alcohol; it

can also be obtained from carvol and ammonium formate (see Abstr., 1892, 499). The *phenylhydrocarvyllthiocarbamide*,



obtained from the compound of either origin, melts at 125—126°, and the *acetyl* derivative, $\text{C}_{10}\text{H}_{17}\cdot\text{NHAc}$, at 132°. The *hydrochloride*, $\text{C}_{10}\text{H}_{17}\text{NH}_2\cdot\text{HCl}$, melts at 190° with decomposition (see below), the *benzoyl* derivative at 181—182°, and the *phenylhydrocarvyllcarbamide* at 191°. Dextro- and lævo-dihydrocarvyllamine and their derivatives have similar properties. The inactive (racemic) *phenylhydrocarvyllthiocarbamide* melts at 119°.

On heating dihydrocarvyllamine hydrochloride, boiling the base with dilute sulphuric acid, heating it with potassium hydrogen sulphate, or warming the normal nitrite with water, terpinene, admixed with a small quantity of cymene, is obtained.

When a concentrated aqueous solution of dihydrocarvyllamine hydrochloride is warmed with a solution of sodium nitrite, dipentene (inactive limonene) is formed, probably through the intermediary production of an alcohol; the conversion of carvol into limonene has therefore been accomplished. In the reaction last described, the formation of a nitrite which gave dihydrocarveol on hydrolysis with potash was also observed.

Terpineol and dihydrocarveol are therefore closely related, and appear to differ only in the positions of their hydroxyl groups. Terpineol is a tertiary alcohol, and dihydrocarveol a secondary alcohol.

A. R. L.

Oxidation of Terpene Derivatives. By O. WALLACH (*Annalen*, 275, 145—183).—Carvol and dihydrocarveol are readily oxidised when shaken with potassium permanganate solution in the cold, and on adding sodium hydroxide and iodine to the filtered liquid, iodoform separates; if bromine instead of iodine is used, carbon tetrabromide is precipitated. Terpinol, limonene, and other terpene derivatives likewise yield carbon tetrabromide under similar treatment. When bromine is added to dilute solutions of dehydracetic and mesitonic acids containing alkali (an excess of alkali must in all cases be employed), carbon tetrabromide is obtained, and it is also formed by treating extremely dilute alkaline solutions of levulinic acid, mesitonic acid, and acetone with bromine. It is therefore suggested that the formation of carbon tetrabromide is brought about in compounds containing the acetyl group, when the dilution is such that the bromine can interact with the nascent bromoform, the latter being precipitated from more concentrated solutions. With compounds which, in relatively more concentrated solutions, give rise to the formation of carbon tetrabromide, it is concluded either that no ready-formed acetyl group is present, but that such a complex is produced during the reaction, which is sufficiently prolonged to favour the precipitation of carbon tetrabromide, or that the compound has an atomic configuration which renders it capable of directly forming carbon tetrabromide.

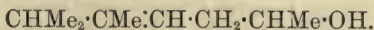
When terpineol is carefully oxidised in the cold with potassium permanganate, the aqueous solution gives the iodoform and carbon

tetrabromide reactions, and it therefore seemed likely that the product was a ketonic acid. It proves, however, to be an indifferent *compound*, $C_{10}H_{20}O_3$, and, in view of Wagner's investigations, may be a trihydroxyterpine; it crystallises from alcoholic ether in transparent crystals, melts at $121-122^\circ$, boils at $170-180^\circ$ (11 mm.), and is almost insoluble in ether. When this substance is further oxidised with chromic acid and dilute sulphuric acid, it is converted into a compound $C_{10}H_{16}O_3$, which crystallises from water in monoclinic pyramids, melts at $62-63^\circ$, and boils at about 330° .

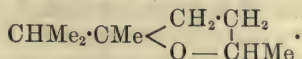
Dihydrocarveol, on oxidation, behaves in a manner similar to terpinol; the product has not yet been obtained in the crystalline condition. On oxidation with potassium permanganate, carvol yields a neutral *compound*, $C_{10}H_{12}O_5$, soluble in water, and two *acids* melting at about 185° and 100° respectively.

The resemblance of the reactions of fenchone and camphor has already been noted (Abstr., 1891, 1086; 1892, 1236). It is now found that when fenchone is gently heated with phosphoric anhydride (under which circumstances camphor yields cymene) it is converted into *metacymene* (*metamethylisopropylbenzene* ?); it boils at $175-176^\circ$, has a sp. gr. at $20^\circ = 0.862$, and a specific refractive power $[n]_D = 1.49222$. On oxidation with potassium permanganate, it yields an unsaturated acid, $C_{10}H_{10}O_2$, which is volatile with steam, and melts at 99° , also an *acid* which is not volatile with steam, melts at $123-124^\circ$, and has the composition of a hydroxypropylbenzoic acid; on oxidation with dilute nitric acid, metatoluic acid is formed. The production of isocymene has been observed from other terpene derivatives, but its formation from camphor and zinc chloride (Armstrong and Miller, Abstr., 1884, 44) is probably due to a secondary reaction.

Methylheptylene ketone (Abstr., 1893, i, 106) is obtained somewhat less readily from α -thujaketonic acid than from the β -acid; this ketone has probably the constitution $CHMe_2 \cdot CMe \cdot CH \cdot CH_2 \cdot CMe$. It is converted into dihydro- ψ -cumene, C_9H_{14} , when heated on the water-bath with zinc chloride; the latter boils at about 160° , has a sp. gr. at $19^\circ = 0.844$, and a specific refractive power $[n]_D = 1.47194$. When the methylheptylene ketone is reduced with sodium and alcohol, an unsaturated *alcohol* (see also *loc. cit.*), boiling at $185-187^\circ$, is formed; it has a sp. gr. at $21^\circ = 0.848$, and a specific refractive power $= 1.4458$. It combines with bromine and hydrogen bromide, and is probably represented by the constitutional formula



When the alcohol is heated with zinc chloride or dilute sulphuric acid, it yields, instead of a hydrocarbon, an isomeric saturated *oxide*, closely resembling cineole, and having the odour of peppermint; it boils at $149-151^\circ$, has a sp. gr. at $20^\circ = 0.847$, and a specific refractive power $[n]_D = 1.42693$; its constitution is probably



The isomerism of α - and β -thujaketonic acids needs further investi-

gation. Semmler (this vol., i, 108) believes them to be stereoisomerides, but the author gives reasons for not accepting the constitutional formula proposed by him. Accepting the above formulæ for methylheptylene ketone, the constitution of the thujaketonic acids is most probably $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{C}(\text{CHMe}_2)\cdot\text{CH}_2\cdot\text{COOH}$.

When the ketone (methylhexylene ketone), $\text{C}_8\text{H}_{14}\text{O}$, boiling at $173\text{--}174^\circ$ (Abstr., 1890, 1314), is treated with sodium and alcohol, an unsaturated alcohol, $\text{C}_8\text{H}_{16}\cdot\text{OH}$, is obtained; this boils at $174\text{--}176^\circ$, has a sp. gr. = 0.85, and a specific refractive power $[\eta]_D = 1.44889$. When the alcohol is warmed with dilute sulphuric acid, it is converted into an isomeric oxide, which boils at $127\text{--}129^\circ$, has a sp. gr. 0.85, and a specific refractive power $[\eta]_D = 1.4249$. The analogy of the compounds $\text{C}_9\text{H}_{18}\text{O}$ and $\text{C}_8\text{H}_{16}\text{O}$ is therefore complete.

When bromine is added to thujone diluted with light petroleum, a tribromo-derivative, $\text{C}_{10}\text{H}_{13}\text{Br}_3\text{O}$, is formed; it crystallises in monoclinic plates, melts at $121\text{--}122^\circ$ with decomposition, and slowly undergoes decomposition at the ordinary temperature. The author has obtained the same compound from Semmler's tanacetone (*loc. cit.*), and thereby proves this chemist's observation that tanacetone and thujone are identical.

When thujone is treated with a solution of bleaching powder, or of alkaline hypobromite, a saturated *bibasic acid*, $\text{C}_{10}\text{H}_{16}\text{O}_4$, which melts at $146\text{--}147^\circ$ with decomposition, is formed, together with a smaller amount of Semmler's liquid acid (tanacetogenic acid). Semmler has privately informed the author that he has since obtained the same result.

The fraction of thuja oil boiling above 220° yields an inactive *oxime*, melting at $93\text{--}94^\circ$; it is probably identical with inactive carvole.

A. R. L.

The Constitution of Camphor. By P. CAZENEUVE (*Bull. Soc. Chim.* [3], 9, 38—45).—This paper discusses the evidence generally for the constitution of camphor, and concludes in favour of Kekulé's formula as modified by Haller.

W. T.

Bromocamphoric Anhydride and Camphoric acid. By O. ASCHAN (*Ber.*, 26, 1639—1645).—Bromocamphoric anhydride, when reduced with zinc-dust and acetic acid, yields mainly camphoric anhydride (m. p. $217\text{--}218^\circ$), which is precipitated from the acetic solution by the addition of water. The filtrate contains a camphoric acid, which crystallises in tufts of slender needles, melts at $120\text{--}125^\circ$, and when crystallised three or four times from dilute alcohol, is converted into a modification which crystallises in rhombohedra or plates, melts at $172\text{--}173^\circ$, and is probably isocamphoric acid. The author was unable to isolate ordinary camphoric acid from the product of the reduction of bromocamphoric anhydride (Rupe and Maull, this vol., i, 524).

When camphoric chloride is treated with 2, 3, or 4 atoms of bromine, only 1 atom of bromine is introduced into the molecule, and by treating the product with water or formic acid, bromocamphoric anhydride is obtained. The substance prepared in this way is crystallo-

graphically identical with that prepared from camphoric acid or its anhydride.

Bromocamphoric anhydride, when treated with alcoholic potash, is converted into camphanic acid; when heated with aniline on the water-bath, it yields phenylamidocamphoric anhydride; when boiled with potassium acetate and acetic acid, it gives a quantitative yield of camphanic acid; and, when melted with potassium acetate, it yields acetic anhydride and potassium camphanate. E. C. R.

Ethyl Hydrogen Camphorate. By S. HOOGEWERFF and W. A. VAN DORP (*Rec. Trav. Chim.*, **12**, 23—25).—This substance, obtained by adding sodium ethoxide to an alcoholic solution of camphoric anhydride, or by passing gaseous hydrogen chloride into an alcoholic solution of the acid, has been obtained in rhombic prisms, melting, in the first case, at 46—47.5°, in the second at 47—48.5°; previously it was known only as an oil. C. F. B.

Substituted Isoimides of Camphoric acid. By S. HOOGEWERFF and W. A. VAN DORP (*Rec. Trav. Chim.*, **12**, 12—22).—*Camphor-methylimide*, prepared by heating camphormethylamic acid, forms colourless crystals, melts at 40—42°, and boils at 270°. *Camphor-benzylimide*, prepared by heating benzylammonium camphorbenzylamate, forms colourless crystals melting at 58—62°.

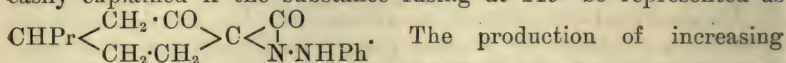
When substituted camphoramides are heated at 80° with acetic chloride (3 parts), or at 100—110° with phosphorus oxychloride (2 parts), substances isomeric with the imides are obtained. These *isoimides* remain as oils when the product is treated with carbon bisulphide, to remove the excess of chloride, and can then be purified by solution in ether, precipitation as hydrochloride by means of gaseous hydrogen chloride, decomposition of the hydrochloride with soda, and extraction of the isoimide with ether. *Camphormethylisoimide* forms small, tabular crystals which melt at 134—136°, and at a higher temperature are transformed into the imide. Water regenerates the amic acid; methylamine gives *camphordimethyldiamide*, $C_8H_{14}(CONHMe)_2$, as a crystalline powder melting at 244—247°. *Camphorethylisoimide* forms tables melting at 80—82°; *camphorbenzylisoimide* small tables melting at 63—66°. Isoimides of other orthodicarboxylic acids could not be prepared, except in the case of phthalic acid, of which an isoimide was probably obtained, but not in a pure state.

The substituted camphorimides are usually assumed to have the constitution $C_8H_{14} \begin{smallmatrix} CO \\ < > \\ CO \end{smallmatrix} NR$, and the structure of the isoimides is hence probably represented by $C_8H_{14} \begin{smallmatrix} C(NR) \\ < > \\ CO \end{smallmatrix} O$. If this is so, then phthalisoimide will be the intermediate compound discussed in this vol., i, 268, and should therefore yield orthocyanobenzoic acid when treated with ammonia; this the above-mentioned impure phthalisoimide actually does. Similarly, it was found possible to obtain camphorisoimide itself, although not in a pure state, and to convert it, by means of ammonia, into an acid, $CN \cdot C_8H_{14} \cdot COOH$.

C. F. B.

Action of Phenylhydrazine on Camphoric Anhydride and the Ethereal Salts of Camphoric acid. By C. FRIEDEL and A. COMBES (*Bull. Soc. Chim.* [3], 9, 27—30).—Camphoric anhydride reacts with phenylhydrazine when heated with it for a long time on the water-bath or for a few minutes at 180—200°, yielding colourless crystals, insoluble in cold, slightly soluble in hot water, melting at 119°, and having the composition $C_{16}H_{20}N_2O_2$. There is no action at the ordinary temperature.

Diethylic camphorate is not acted on by phenylhydrazine when boiled therewith for several hours. Monethylic camphorate, prepared by the direct etherification of camphoric acid by alcohol and hydrogen chloride, yields the compound $C_{16}H_{20}N_2O_2$, as Haller has shown for the methylic salt (compare Brühl and Braunschweig, this vol., i, 277); whereas the monethylic camphorate, prepared by partial hydrolysis of the diethylic salt, is not acted on. Hence the dicarboxylic formula for camphoric acid must be rejected. The difference of the reaction with phenylhydrazine in the two cases is easily explained if the substance fusing at 119° be represented as



The production of increasing quantities of camphorimide (m. p. 245°), and of benzene when the mixture of phenylhydrazine and camphoric anhydride is maintained for some minutes at 200°, renders the formula given more probable if camphoric acid be admitted to be a ketohydroxymonocarboxylic acid (see also Brühl, *Abstr.*, 1892, 1100; and Friedel, *Abstr.*, 1892, 500).

W. T.

Preparation of Cantharidin. By E. DIETERICH (*J. Pharm.* [5], 27, 375—377; from *Helpfenberger Ann.*, 1892, 1).—Coarsely powdered cantharides (1000 grams) are placed in a porcelain vessel, and a mixture of ethylic acetate (1500 grams; sp. gr. = 0.902) and sulphuric acid (20 grams; sp. gr. = 1.838) is added, the whole stirred thoroughly, and left for two days. (The object of the sulphuric acid is to decompose a compound of cantharidin contained in the insects.) Barium carbonate (40 grams) is then added, and stirred in, and the whole is extracted with ethylic acetate in a reflux extraction apparatus. The residue, after distilling off the ethylic acetate from the extract, is left for eight days in a porcelain capsule to allow the cantharidin to crystallise. Fats are removed by boiling with light petroleum (200 grams; sp. gr. = 0.740), and washing the residue two or three times with hot light petroleum (30 grams each time). Resins are now removed by pulverising the residue, warming with alcohol of 90° (300 grams), setting aside, pouring off the liquid the next day, and washing the residual crystals with alcohol (20 grams) and then with ether (20 grams; sp. gr. = 0.720). The cantharidin is now sufficiently pure for making plasters; to further purify it, it may be heated (15 grams) for two hours at 40—50° with ethylic acetate (150 grams) and animal charcoal (1 gram), and the solution filtered and allowed to crystallise. The yield varies from 0.3 to 1.03 per cent. of the insects taken.

C. F. B.

Scoparin. By G. GOLDSCHMIEDT and F. v. HEMMELMAYR (*Monatsh.*, 14, 202—222).—This substance, together with spartein, was discovered by Stenhouse in the aqueous extract of *Spartium scoparium*. In order to purify it, it was repeatedly dissolved in boiling water, from which it separates, on cooling, as a gelatinous mass, and crystallised from 70 per cent. alcohol. It forms nodular aggregates of small, yellow needles, melts at from 202° to 219°, accordingly as it is heated slowly or quickly, and seems to have the composition $\text{OH} \cdot \text{C}_{19}\text{H}_{16}\text{O}_8 \cdot \text{OMe} + 5\text{H}_2\text{O}$ (Stenhouse, $\text{C}_{21}\text{H}_{22}\text{O}_{11}$). It reduces Fehling's solution, and gives, with ferric chloride, a violet-blue coloration which quickly becomes dark-brown, or is changed to yellowish-brown by sodium carbonate. A barium derivative, $(\text{C}_{20}\text{H}_{19}\text{O}_{10})_2\text{Ba} + 2\text{H}_2\text{O}$, was obtained by boiling an aqueous solution of scoparin with barium carbonate. When heated with hydriodic acid, scoparin yields 1 mol. of methylic iodide, and at the same time loses 1 mol. of water, giving a substance, $\text{C}_{19}\text{H}_{14}\text{O}_8$, which forms a bright yellow, amorphous powder, becomes dark at 175°, and melts with decomposition above 200°. It yields a *monacetyl derivative* forming nearly white crystals, melting at 230—236° when still impure, and a *monethyl derivative* crystallising in tiny, bright yellow needles melting with decomposition at 272°. It seems not to be a glucoside, for when boiled with dilute sulphuric acid, no sugar could be detected in the solution; an insoluble, brownish-yellow substance, $\text{C}_{20}\text{H}_{16}\text{O}_8 + 2\frac{1}{2}\text{H}_2\text{O}$ (?), was, however, formed. When scoparin is boiled with absolute alcohol, it is converted into Stenhouse's "apparently allotropic" modification; this forms a yellow, crystalline powder, melts at 235°, and seems to have the same percentage composition as scoparin itself. C. F. B.

Urson. By W. H. GINTL (*Monatsh.*, 14, 255—269).—This substance occurs, together with arbutin, in the leaves of the red bear berry (*Arbutus uva ursi*). It has the constitution $\text{C}_{30}\text{H}_{48}\text{O}_3 + 2\text{H}_2\text{O}$, possibly $\text{O} < \begin{smallmatrix} \text{C}_{15}\text{H}_{24} \\ \text{C}_{15}\text{H}_{23}(\text{OH}) \end{smallmatrix} > \text{O}$ containing two sesquiterpene residues, and melts at 263—266°, not, as Hlasiwetz says, at 198—200°. When it is dissolved in acetic anhydride, and concentrated sulphuric acid added to the solution when cold, a red coloration is produced which rapidly becomes violet, then blue, and finally green; if a drop of water is added immediately after the sulphuric acid, the red colour at once changes to green. Urson does not react with hydroxylamine or phenylhydrazine; it contains no methoxyl group; but it does contain an hydroxyl group, for it yields a *monacetyl derivative* which forms white needles melting at 264°, and a *monobenzoyl derivative*, as a yellowish, amorphous powder, melting at 214°. The action of bromine, permanganate, chromic acid, and fused potash was also studied, but no very definite results were obtained. When reduced with hydriodic acid and phosphorus at 360°, or, better, when distilled with zinc-dust in a stream of hydrogen, urson yields small quantities of a substance, $\text{C}_{15}\text{H}_{24}$, probably a sesquiterpene, which boils at 256—267°, is feebly dextrorotatory, and gives a red coloration with

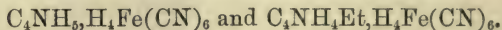
strong sulphuric acid, and a dark-brown one with acetic anhydride and a drop of sulphuric acid.

C. F. B.

New Naturally-occurring Nitrogenous Organic Acid. By F. KLINGEMANN (*Annalen*, **275**, 89—91).—Stahlschmidt (*Annalen*, **187**, 177; **195**, 365) obtained an acid $(C_9H_7O_2)_n$, which he named polyporic acid, from a certain fungus occurring on diseased oaks. This fungus was perhaps *Polyporus igniarius*, and it seems probable that the acid was not a normal constituent but a pathogenic one. The author finds that *Polyporus igniarius* contains an acid which differs from polyporic acid, but may, perhaps, under certain conditions, be convertible into it. The new acid dissolves in alkalis with a deep brown colour, and on analysis gives values agreeing best with the formula $C_{36}H_{39}N_3O_{16}$.

A. R. L.

The Basic Properties of Pyrroline Derivatives. By G. CIAMCIAN and C. U. ZANETTI (*Ber.*, **26**, 1711—1714).—Pyrroline, 1-ethylpyrroline, 2:5-dimethylpyrroline, and other homologues of pyrroline dissolve in hydrochloric acid, and the solutions give precipitates with the reagents generally used in precipitating alkaloids, as, for example, phosphomolybdic acid; particularly well-characterised are the *ferrocyanides* of pyrroline and 1-ethylpyrroline,



An alkali does not, however, regenerate the original pyrroline from these compounds, but only resinous substances, probably polymerides. On the other hand, ketonic derivatives of pyrroline do give salts from which the original substance may be regenerated. Of these salts there were prepared and analysed the *hydrochloride* and *aurochloride* of 2:5-dimethyl-3-acetylpyrroline and of 2:4-dimethyl-5-acetylpyrroline; and the *aurochloride* of 2:4-dimethyl-3:5-diacetylpyrroline and of 2:5-dimethyl-3:4-diacetylpyrroline, as well as the *hydrobromide* of this last substance, and a *dibromo-additive compound* of the hydrobromide. Pyrrolines, although they do thus form salts, are but feebly basic; this is, however, no argument for their containing *pentavalent* nitrogen, for many other compounds, in which Bamberger does not hesitate to assume the presence of *trivalent* nitrogen, have equally feeble basic properties.

C. F. B.

Piperidine Bases of the β -Series. By C. STOEHR (*J. pr. Chem.* [2], **48**, 17—18).—The following additions are to be made to the author's previous paper on this subject (*Abstr.*, 1892, 628):— β -Methylpiperidine platinochloride, $(C_6H_{13}N)_2, H_2PtCl_6$, crystallises in long, red prisms, dissolves sparingly in water, and melts at 207° with much evolution of gas; its crystallography is given (compare Hesekei, *Abstr.*, 1885, 812). β -Ethylpiperidine aurochloride, $C_7H_{15}N, HAuCl_4$, forms lustrous, rhombohedral crystals, whose measurements are given.

A. G. B.

Conversion of the Indoles into Quinolines. By A. FERRATINI (*Ber.*, **26**, 1811—1815).—Both the trimethyltetrahydroquinoline and

the trimethyldihydroquinoline obtained from indole (this vol., i, 227) are decomposed by phosphorus and hydriodic acid at 230° yielding methylic iodide and dimethyltetrahydroquinoline, which can be isolated by means of its crystalline hydriodide. The free base boils at 234—235°, and yields a hydrochloride of the composition $C_9NH_5Me_2.HCl$, which melts at 198—199°. When this substance is distilled over zinc-dust, hydrogen is evolved and a yellow oil produced. A small amount of 2':3'-dimethylindole is formed by the distillation, and is removed by treating the oil with hydrochloric acid, in which the indole compound is insoluble, whilst unaltered dimethyltetrahydroquinoline can be removed by the action of nitrous acid. The base thus prepared boils at 263—266°, and is identical in composition and properties with 2':4'-dimethylquinoline. When an indole is converted into a quinoline derivative, then, by the action of methylic iodide, the carbon atom which enters the pyrroline ring takes up the 3'- or meta-position relatively to the nitrogen atom. The tetrahydro-2':4'-dimethylquinoline obtained from indole is, however, not identical with that prepared synthetically. The explanation of this remarkable circumstance may perhaps be found in the fact that 2':4'-dimethyltetrahydroquinoline contains two asymmetric carbon atoms, $C_6H_4 \begin{smallmatrix} CHMe \cdot CH_2 \\ \backslash \quad / \\ NH - CHMe \end{smallmatrix}$, so that it is possible that the two known 2':4'-dimethyltetrahydroquinolines are stereo-isomerides derived from the same dimethylquinoline.

A. H.

Constitution of Cycloid Systems. By W. MARCKWALD and others (*Annalen*, 274, 331—376).—The author has previously brought forward certain facts (Abstr., 1890, 1004) connected with Skraup's quinoline synthesis which are only to be explained by the adoption of Kekulé's benzene formula; he maintains that this formula has been disproved neither by v. Baeyer nor by Zincke. Representing naphthalene by Erlenmeyer's and Graebe's formula, and quinoline by Körner's formula, the positions 1:2 and 3:4 are completely different from the position 2:3, whereas the formulæ of Claus and of Bamberger do not indicate such a difference in these positions, it being in the latter cases merely a question of relative situation. On these lines, the following experiments are in accordance with Erlenmeyer and Graebe's formula for naphthalene and Körner's formula for quinoline; they also show that the existence of para-bonds in benzene is extremely improbable.

Dinitrotoluenesulphonic acid $[Me:(NO_2)_2:SO_3H = 1:2:6:4]$ does not yield the diamido-compound on reduction with ammonium sulphide as Schwanert states (this Journal, 1877, ii, 612), but under these circumstances the *nitro-amidosulphonic acid* is formed; this crystallises in delicate needles, and is sparingly soluble in water. The *potassium* and *calcium* salts are anhydrous; the *barium* salt crystallises with $2\frac{1}{2}H_2O$, and the *silver* salt with $\frac{1}{2}H_2O$. On reducing the dinitro-compound with tin and hydrochloric acid, the diamidotoluenesulphonic acid agreeing with Schwanert's description is formed. It yields by Skraup's reaction 1-methyl-2-amidoquinoline-4-sulphonic

acid, which crystallises from water in yellowish-red needles containing $1\text{H}_2\text{O}$; the sodium and calcium salts form yellow, anhydrous needles, the barium and silver salts crystallise with $2\text{H}_2\text{O}$, and the copper salt crystallises with $1\text{H}_2\text{O}$.

1:2'-Dimethyl-2-amidoquinoline-4 sulphonic acid is obtained from the above diamidotoluenesulphonic acid by the Doebner-Miller reaction (paraldehyde and hydrochloric acid); it crystallises from hot water in bright yellow, thick needles containing $2\text{H}_2\text{O}$. The sodium, potassium, calcium, silver, and lead salts are anhydrous; the barium salt crystallises with $4\text{H}_2\text{O}$, and the copper salt with $1\text{H}_2\text{O}$. The two above-described amidoquinoline derivatives remain unaltered when further treated either by the Skraup or the Doebner-Miller reactions because, according to the author, single bonds exist between the 2:3-positions in each (Körner's formula).

Dinitroparatoluic acid [$\text{Me}:(\text{NO}_2)_2:\text{COOH} = 1:2:6:4$] (Abstr., 1892, 177) crystallises with 1 mol. H_2O , and forms a sulphate which is sparingly soluble in water, and crystallises with 3 mols. H_2O .

1-Methyl-2-amidoquinoline-4-carboxylic acid is obtained from the diamidotoluic acid by Skraup's reaction; it forms sulphur-yellow crystals containing $1\frac{1}{2}\text{H}_2\text{O}$, and decomposes without melting at 270° ; the silver salt, the hydrochloride, the platinochloride, and other salts were prepared; the acetyl derivative, $\text{COOH}\cdot\text{C}_9\text{NH}_2\cdot\text{Me}\cdot\text{NHAc}$, forms bright grey, pulverulent crystals, does not melt at 300° , and is hydrolysed into the amido-compound by cold acids. When the last-described methylamidoquinolinecarboxylic acid is distilled, 1-methyl-2-amidoquinoline passes over at 304° ; it crystallises in white prisms, melts at 129° , and remains unaltered when treated by Skraup's reaction; the picrate, chromate, and platinochloride were prepared.

1:2'-Dimethyl-2-amidoquinoline-4-carboxylic acid is obtained by treating the above-mentioned diamidoparatoluic acid by the Doebner-Miller reaction; it forms small, golden-yellow crystals, and decomposes at a high temperature without melting; the silver salt, the hydrochloride and other salts, as well as the acetyl derivative, are described; 1:2'-dimethyl-2-amidoquinoline is obtained by distilling the dimethylamidoquinolinecarboxylic acid; it forms long, colourless, lance-shaped crystals, and melts at 104° ; the picrate, platinochloride, and dichromate were prepared.

Benzoparaphenanthroline, $\begin{array}{c} \text{CH}-\text{N}^1 \\ | \\ \text{CH}\cdot\text{CH}^2 \end{array} > \text{C}_{10}\text{H}_4 < \begin{array}{c} \text{CH}\cdot\text{CH}^3 \\ | \\ \text{N}-\text{CH}^4 \end{array}$, is prepared by

treating 1:4-diamidonaphthalene by Skraup's reaction; it crystallises in transparent, microscopic tables or needles, and melts at 160° ; the picrate melts at 256° .

Paraphenylenediamidepropyl methyl ketone, $\text{C}_6\text{H}_4(\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{COMe})_2$, is obtained by heating paraphenylenediamine with acetylacetone (2 mols.) at 120° . It crystallises from dilute alcohol in yellowish, nacreous leaflets, melts at 175° , and is decomposed into its components when heated with dilute acids or alkalis. All attempts, such as treating it with concentrated sulphuric acid in the cold or at 100° , or by heating it alone, failed to produce a quinoline derivative.

Metaphenylenediimidopropyl methyl ketone, prepared from metaphenylenediamine and acetylacetone, forms bright yellow, lance-shaped crystals, and melts at 135° ; it is converted into *amidodimethylquinoline* [$\text{NH}_2 : \text{Me}_2 = 4 : 2' : 4' \text{ or } 2 : 2' : 4'$] when heated with concentrated sulphuric acid at 100° , or when boiled with glacial acetic acid; the new compound is an oil boiling above 300° , and forming a hydrate, with $2\text{H}_2\text{O}$, which crystallises in yellowish needles; when heated for a long time at 120° , it yields a resinous mass from which an anhydrous modification is obtained on crystallisation from light petroleum; it melts at $94\text{--}100^{\circ}$, and is reconverted into the oily modification on exposure to the air. The *salts* of the base are of a yellow to red colour; the *picrate* melts at $215\text{--}217^{\circ}$; the *acetyl* derivative forms yellowish needles, and melts at 212° .

Phenyldimethylquinolinethiocarbimide, $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_{11}\text{NH}_{10}$ is obtained by boiling together alcoholic solutions of the amidodimethylquinoline and phenylthiocarbimide; it is a yellow, crystalline powder, melts at $173\text{--}174^{\circ}$, and has only weak basic properties; the corresponding *paratolyl* derivative, $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_{11}\text{NH}_{10}$, melts at 142° .

When the last-described amidodimethylquinoline is treated with acetylacetone, a syrupy compound, $\text{C}_{11}\text{NH}_{10} \cdot \text{NMe} \cdot \text{CH}_2\text{Ac}$, is formed, and this, on being heated with concentrated sulphuric acid, is reconverted into the amidodimethylquinoline. When, however, the amidodimethylquinoline is treated by Skraup's reaction, *dimethylphen-*

anthroline, $\begin{array}{c} \text{CH}-\text{N} \\ | \quad | \\ \text{CH}-\text{CH} \end{array} \begin{array}{c} 3 \text{ or } 1 \\ 1 : 3 \end{array} > \text{C}_9\text{NH}_3\text{Me}_2$, is obtained; it forms white crystals,

and melts at $106\text{--}107^{\circ}$; and the *picrate* forms lustrous, yellow needles, and commences to decompose at 230° without melting.

A. R. L.

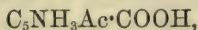
Oxidation of Parahydroxyquinoline. By O. ROSENHEIM and J. TAFEL (*Ber.*, 26, 1501—1513).—*Pyridylglycerolcarboxylic acid*, $\text{COOH} \cdot \text{C}_5\text{H}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{COOH}$, is prepared by the action of calcium hypochlorite in aqueous solution at 0° on parahydroxyquinoline; it is crystalline, and sparingly soluble in cold water, but dissolves readily on heating, and gives a yellow coloration with ferric chloride. The *calcium* and *silver salts* are crystalline; the *potassium salt* forms a syrup; the *lead* and *copper salts* are sparingly soluble. The acid is not acted on by nitrous acid, or hydroxylamine, or by boiling it with water or dilute (10 per cent.) sulphuric acid.

On treating the calcium salt with hydrochloric acid, the *acid lactone*, $\text{C}_9\text{H}_7\text{NO}_5$, is obtained; it crystallises from water in large, thin plates, melts at about 210° with decomposition, and gives a yellow coloration with ferric chloride. The same compound is also formed by the action of calcium hypochlorite on acetylparahydroxyquinoline, showing that the resolution of the quinoline ring occurs at the position of the hydroxyl group. The *ammonium salt* is crystalline; the *calcium* and *silver salts* are deposited in needles; the *copper*, *zinc*, *cadmium*, *mercury*, and *lead salts* are sparingly soluble and crystalline. The *ethyl salt* is deposited from water in groups of colourless

needles, and melts at 135—136° with evolution of gas. The *methylic salt* crystallises in prisms melting at 152°. The *acetyl derivative* is deposited from water in long, thick needles, melts at 177°, and gives no coloration with ferric chloride. The lactonic acid is scarcely acted on by nitric acid or potassium permanganate, but yields quinolinic acid on oxidation with sulphuric acid and potassium dichromate.

On heating the lactonic acid with ammonia in a sealed tube for two hours at 150—160°, and treating the crystalline product with sulphuric acid, an acid, $C_5H_6N_2O_3$, is formed which is deposited from glacial acetic acid in colourless, paper-like masses, darkening at 302°, melting at 321°, and giving a yellowish-red coloration with ferric chloride. This acid appears to be the analogue of isocarbostyryl-carboxylic acid, and may perhaps therefore have the formula $C_5NH_3 < \begin{smallmatrix} CO \cdot NH \\ CH : C \cdot COOH \end{smallmatrix}$; its formation indicates that pyridylglycerol-carboxylic acid lactone is probably a δ -lactone. On heating the imido-acid above its melting point, carbonic anhydride is evolved, and a crystalline compound sublimes, which is insoluble in alkalis, and melts at 236—238°.

α -Acetopyridine- β -carboxylic acid (α -acetonicotinic acid),



is prepared by heating pyridylglycerolcarboxylic acid lactone with 5—6 parts of water in a sealed tube at 140°; it crystallises from water in small needles, melts at 127°, and gives no coloration with ferric chloride. The *potassium* and *ammonium salts* are readily soluble and crystalline; the *silver* and *mercurous salts* are sparingly soluble. The *ethylic salt* is an oily liquid, but forms a *hydrochloride*, crystallising in colourless plates which melt at 133—134°.

Acetonicotinic acid oxime anhydride, $C_5NH_3 < \begin{smallmatrix} CO \cdot O \\ -CMe \end{smallmatrix} > N$, is obtained by the action of hydroxylamine hydrochloride on the acid, and crystallises in long, slender needles; it melts at 171°, and dissolves in alkalis or in concentrated hydrochloric acid.

Acetonicotinic acid phenylhydrazone anhydride, $C_5NH_3 < \begin{smallmatrix} CO \cdot NPh \\ CMe : N \end{smallmatrix} >$, is formed from phenylhydrazine hydrochloride and acetonicotinic acid, and crystallises from alcohol in colourless needles melting at 121°. The compound dissolves in concentrated mineral acids with a yellow colour, but is stable towards alkalis.

Acetonicotinic acid is scarcely affected by potassium permanganate even on heating, but by treatment with nitric acid, quinolinic acid is formed.

J. B. T.

Isomerides and Congeners of "Analgen," Ethoxy-4-benzoylamidoquinoline. By G. N. VIS (*J. pr. Chem.* [2], 48, 24—30).—"Analgen" is the trade name for ethoxy-4-benzoylamidoquinoline, a compound employed as an antineurotic. This substance is made from 1-ethoxynitroquinoline (Abstr., 1892, 1104) by reducing it to the amido-derivative by means of iron, and benzolysing by the Schotten-

Baumann method. It crystallises from alcohol, in which it dissolves sparingly; it is insoluble in water, but dissolves in acids, being a feeble base; it cannot be hydrolysed by alkalis or dilute acids. In the organism, analgen is partly entirely broken down and partly decomposed with liberation of ethoxyamidoquinoline, which forms a red-coloured urate in the urine.

Dinitro-1-methoxyquinoline is best prepared by nitrating methoxyquinoline sulphate; in properties it is very similar to the corresponding ethoxy-derivative (*loc. cit.*). *1-Methoxy-4-nitroquinoline* crystallises as its nitrate from the filtrate from the preceding compound; this base melts at 151.5° and dissolves in hot alcohol, but not in water. When reduced in hydrochloric acid solution, it yields the corresponding amido-derivative, which crystallises from alcohol in yellow needles melting at $155\text{--}156^{\circ}$, and from water in crystals containing $1\text{H}_2\text{O}$ and melting at 76° .

1-Methoxy-4-acetamidoquinoline is prepared by treating the amide which has just been described with glacial acetic acid; it crystallises at first in needles, but these soon change into octahedral crystals; the crystals from an aqueous solution contain $1\text{H}_2\text{O}$. It melts at 179° . When it was administered to a dog, it was found to have, in great measure, passed through the system unchanged.

1-Methoxy-4-benzoylamidoquinoline was prepared, in a manner analogous to the ethoxy-derivative; it crystallises in white needles, melts at $268\text{--}269^{\circ}$, and dissolves in hot alcohol. Its salts are easily soluble.

3-Ethoxy-4-nitroquinoline, made by nitrating 3-ethoxyquinoline (b. p. 291°), crystallises in yellow needles; it is practically insoluble in water and has a sweet taste, whereas the 1-derivative is bitter. The *platinochloride* forms orange needles; the *methiodide* crystallises in orange-coloured prisms, and melts at 205° with decomposition.

3-Ethoxy-4-amidoquinoline, prepared by reducing the nitro-derivative, crystallises with $1\text{H}_2\text{O}$ in yellow needles which melt at 76° ; the dry compound melts at $115\text{--}116^{\circ}$. It dissolves in hot alcohol and hot water. The *acetamido*-derivative crystallises in white laminae, melts at $163\text{--}163.5^{\circ}$, and dissolves in hot water. The *benzoylamido*-derivative forms white crystals, melts at 144° , and is fairly soluble in water. The acid radicle is eliminated from each of these two derivatives in the system.

By diazotising the amido-derivative and treating the diazo-compound with cuprous bromide, *3-ethoxy-4-bromoquinoline* was prepared; this crystallises in long, lustrous needles, melts, when dry, at $80\text{--}81^{\circ}$, and dissolves in hot alcohol; the *hydrochloride* forms sparingly soluble, yellow needles, and melts at 235° . The same ethoxybromoquinoline was prepared by treating 3-hydroxy-4-bromoquinoline with caustic soda and ethylic bromide, and thus the 4-position of the bromine atom and *pari passu* of the original nitro-group was verified.

A. G. B.

New Synthesis of Isoquinoline. By C. POMERANZ (*Monatsh.*, **14**, 116—119).—Isoquinoline is formed when benzaldehyde is mixed with amidoacetal, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$, the mixture dried with potassium carbonate, and heated for half an hour at $100\text{--}120^{\circ}$ with 3—4 times its weight of strong sulphuric acid.

C. F. B.

A New Synthesis of Isoquinoline. By A. BISCHLER and B. NAPIERALSKI (*Ber.*, 26, 1903—1908).—When an acidic derivative, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CRO$, of ω -phenylethylamine is heated with phosphorus pentoxide or zinc chloride, it is condensed to a substance that is doubtless a dihydroisoquinoline, $C_6H_4 \begin{smallmatrix} CH_2 \cdot CH_2 \\ | \\ CR : N \end{smallmatrix}$, although a satisfactory proof of this has not yet been obtained. The yield is poor. Phosphorus pentachloride does not effect this condensation; an imido-chloride is formed which undergoes no further change.

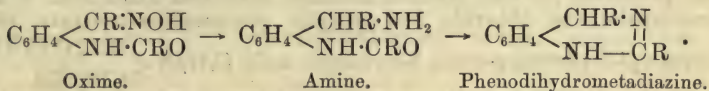
o-Phenylethylamine is obtained by reducing phenylacetoxime with sodium amalgam in alcoholic solution kept acid with acetic acid; it is a colourless liquid boiling at 197—198° under 725 mm. pressure. The *acetyl derivative* (phenylethylacetamide) forms nodular aggregates of white needles, melts at 42—44°, and boils at 305—306° under 725 mm. pressure; it yields by condensation 1'-methyl-dihydroisoquinoline as a yellow oil boiling at 237—242°, the *platinochloride* of which forms yellow crystals. The *benzoyl derivative* (phenylethylbenzamide) forms white plates melting at 113—114°; by condensation, it yields 1'-phenyl-dihydroisoquinoline, which was obtained only as an impure oily product; this, however, yields an orange-coloured, crystalline *platinochloride* melting at 194—195°. The *formyl derivative* (phenylethylformamide) is a colourless oil boiling at 205° under 15 mm. pressure and, under the ordinary pressure at 300° with partial decomposition; it decomposes when an attempt is made to condense it to dihydroisoquinoline. C. F. B.

Isoquinoline Derivatives. By P. FORTNER (*Monatsh.*, 14, 146—164).—When isoquinoline is dissolved in strong nitric acid and the solution added to a mixture of strong sulphuric and fuming nitric acids, and heated on the water-bath, *nitroisoquinoline* [$NO_2 : N = 1 : 2'$ or $4 : 2'$] with $1H_2O$ is formed, and may be separated by adding potash; it crystallises in long, fine, silky, faintly yellowish needles, and melts at 110°. The *hydrochloride* forms yellowish tables which melt at 240°; these are monoclinic, $a : b : c = 1.0024 : 1 : 2.0718$; $\beta = 90' 33'$, and are twinned relatively to the basal plane. The *platinochloride* forms bundles of yellow prisms, decomposing above 300°; the *dichromate*, microscopic, reddish-yellow needles, decomposing at 100°; the *picrate*, lustrous, yellow plates melting at 220°. Nitroisoquinoline also forms *compounds* (1 mol. of each) with *methyl iodide*, as reddish-yellow prisms melting at 195°; with *ethyl bromide*, as almost colourless, lustrous needles melting at 219—220°; and with *benzyl chloride*, as faintly yellowish tables melting at 205°. Nitroisoquinoline is oxidised by permanganate to nitrophthalic acid [$(COOH)_2 : NO_2 = 2 : 3 : 1$ or $2 : 3 : 4$], and this, when heated with bromine (1 mol.) for two hours at 100° in a sealed tube, yields the bromonitroisoquinoline obtained by Edinger and Bossung (*Abstr.*, 1891, 580) by nitrating bromisoquinoline, of which it is only known that the bromine is in the pyridine ring. By reducing nitroisoquinoline with aqueous stannous chloride, *amidoisoquinoline* is obtained; it formed yellowish needles, but was not quite pure, for it melted in one case at 128—130°.

in another at 154°. The *hydrochloride*, with 2HCl, forms colourless needles, melting with decomposition at 200°; the *platinochloride*, with $\frac{1}{2}$ H₂PtCl₆, a yellowish, crystalline precipitate, turning brown at 300°; the *picrate*, a yellow precipitate, decomposing above 200°. By oxidation of a dilute aqueous solution of isoquinoline and boric acid with bleaching powder, and subsequent treatment of the product with ether, a substance was obtained in nearly white needles melting at 218°; it contained chlorine, and when dissolved in hot aqueous potash and reprecipitated with carbonic anhydride, yielded a chlorhydroxyisoquinoline, C₉NH₅Cl.OH, in colourless crystals melting at 238°.

C. F. B.

Phenometadiazine Derivatives. By A. BISCHLER and W. OSER (*Ber.*, 26, 1891—1903).—A new synthesis of these derivatives has been accomplished in the following manner. The oxime of an ortho-acetamidocarbonyl compound is reduced at 15° in alcoholic solution with sodium amalgam, the solution being kept acid with acetic acid; the amine thus formed yields, by condensation with strong hydrochloric acid, zinc chloride, or, better, phosphorus pentoxide, a phenodihydrometadiazine.

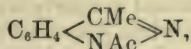


Orthacetamidobenzaldoxime, NHAc.C₆H₄.CH:NOH, obtained from orthacetamidobenzaldehyde and hydroxylamine, forms lustrous, colourless crystals melting at 194°. When reduced, it yields *orthacetamidobenzylamine*, which was obtained as an oil; its *benzoyl derivative* forms small, white, asbestos-like needles melting at 170°. The amine yields, by condensation, *pheno-2-methyldihydrometadiazine*, yellow oil with an odour of mice, boiling at 260—270°, the *hydrochloride* of which forms short, colourless prisms, the *picrate*, stellate groups of orange-yellow needles melting at 163—167°. By successive treatment of the diazine with methylic iodide and potash, *pheno-2 : 3-dimethyldihydrometadiazine* is obtained; it crystallises in small, white needles, and melts at 124—126°. These two diazines are isomeric with the β-methyl- and β-γ-dimethyl-dihydroquinazoline of Gabriel and Jansen (*Abstr.*, 1892, 217).

α-Orthacetamidophenylethylamine, NHAc.C₆H₄.CHMe.NH₂, is obtained as an oil by reducing the oxime of orthacetamidoacetophenone, or, better, the acetic derivative of this; when treated with benzoic anhydride, a *dibenzoyl derivative* of *orthamidophenylethylamine* is obtained in nodular aggregates of colourless needles melting at 156—157°; it was also prepared directly from *α-orthamidophenylethylamine*, obtained as an oil by reducing orthamidacetophenonoxime. This amine also yields a *hydrochloride* in colourless prisms which soften at 187°; a *dihydrochloride* as a white, crystalline powder; a *picrate* in yellow needles melting at 160—170°; and a *diacetic derivative* as colourless, flattened needles melting at 131°. The above-mentioned *α-orthacetamidophenylethylamine* yields, by condensation, *pheno-2 : 4-dimethyldihydrometadiazine* as a brown

fluorescent oil, boiling at 280° under 722 mm. pressure, of which the *picrate* forms lemon-yellow crystals melting at 173°, and the *platino-chloride*, orange-yellow crystals melting with decomposition at 205—206°.

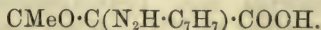
When the oxime of orthacetamidoacetophenone is reduced, much of it is converted into the 1' : 3'-acetylmethylisindazole,



of Auwers and v. Meyenburg (Abstr., 1892, 1376), which is, in fact, obtained directly by the action of hydroxylamine on orthacetamidoacetophenone in neutral or faintly acid solution. It crystallises with 3H₂O, and then melts at 63°; the authors think that its constitution may perhaps be represented by $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CMe} \cdot \text{N} \\ \text{N} \cdot \text{CMe} \end{smallmatrix} > \text{O}$, instead of by the above formula.

C. F. B.

New Synthesis of Pyrazole Derivatives. By A. BISCHLER and W. OSER (*Ber.*, 26, 1881—1890).—More pyrazole derivatives have been prepared by the method already described (this vol., i, 44). Paradiazotoluene chloride and ethylic phenacylacetoacetate yield 1-*paratolyl*-5-*phenylpyrazole*-3-*carboxylic acid*, $\text{C}_7\text{H}_7 \cdot \text{N} < \begin{smallmatrix} \text{N} = \text{C} \cdot \text{COOH} \\ \text{CPh} \cdot \text{CH} \end{smallmatrix}$, in crusts of lustrous, yellow prisms melting at 194—195°, together with the α -*paratolylhydrazone* of $\alpha\beta$ -diketobutyric acid,



Orthodiazotoluene chloride yields the corresponding *orthotolyl* compounds, in crusts of orange-yellow prisms melting at 170—171°, and as lustrous, orange-yellow needles melting at 135° respectively, and, in addition to these, the tolueneazo-compound of the first, $\text{C}_7\text{H}_7 \cdot \text{N} < \begin{smallmatrix} \text{N} = \text{C} \cdot \text{COOH} \\ \text{CPh} \cdot \text{C} \cdot \text{N}_2 \cdot \text{C}_7\text{H}_7 \end{smallmatrix}$, as orange-red needles melting at 179°.

Diazobenzene chloride and ethylic acetonylacetoacetate yield 1-*phenyl*-5-*methylpyrazole*-3-*carboxylic acid*, with 1H₂O, in groups of flattened, colourless, lustrous needles, melting at 106° (when anhydrous at 134—135°), together with the α -phenylhydrazone of $\alpha\beta$ -diketobutyric acid. Diazobenzene chloride and ethylic desylacetoacetate yield 1 : 4 : 5-*triphenylpyrazole*-3-*carboxylic acid* in stellate groups of lustrous, yellow needles melting with decomposition at 245°; this substance, when heated, loses carbonic anhydride and the residue distils at 400°; from the distillate, 1 : 4 : 5-*triphenylpyrazole* is obtained in nodular aggregates of small, white, silky needles melting at 212°. Diazobenzene chloride and phenacylacetic acid in alkaline solution yield a small quantity of a substance which crystallises in dark red prisms, and melts at 132°, together with a substance, probably 1 : 5-*diphenyl*-3-*acetylpyrazole*, which crystallises in nodular aggregates of flattened nacreous needles and melts at 88°.

C. F. B.

Pyrazolone from Ethylic Acetylenedicarboxylate. By R. v. ROTHENBURG (*Ber.*, 26, 1719—1722).—Ethylic acetylenedicarboxylate reacts with hydrazine hydrate in absolute alcoholic solution even more readily than the oxalacetate, and yields ethylic pyrazolone-3-carboxylate, together with some pyrazolone-3-carboxylic hydrazide, and a small quantity of a substance which crystallises in white needles, and melts at 87°; it then becomes solid, and melts again at 242°. The pyrazolonecarboxylate was converted into pyrazolone by the stages already described (this vol., i, 180). C. F. B.

Pyrazolone from Ethylic Propiolate. By R. v. ROTHENBURG (*Ber.*, 26, 1722—1724).—When ethylic propiolate in absolute alcoholic solution is treated with hydrazine hydrate, pyrazolone is formed to the extent of 25—30 per cent. of the theoretical yield, but it cannot readily be isolated. From the acid solution were prepared various salts, of which the *silver salt* has the composition $C_3H_4N_2O, C_3H_3AgN_2O$. An aqueous solution treated successively with sodium nitrite and silver nitrate gives a *silver salt*, $\begin{matrix} N=CH \\ | \\ NH \cdot CO \end{matrix} > C \cdot NOAg$. A feebly alkaline solution, treated with paradiazotoluene sulphate, yields *pyrazolone-4-parazotoluene*, $\begin{matrix} N=CH \\ | \\ NH \cdot CO \end{matrix} > C \cdot N \cdot NH \cdot C_6H_4Me$, which crystallises in tiny, reddish-purple plates, melting at 219°. C. F. B.

Phenylpyrazolidine. By A. MICHAELIS and O. LAMPE (*Annalen*, 274, 316—331; compare *Abstr.*, 1892, 355).—Phenylpyrazolidine (*loc. cit.*) has a sp. gr. of 1.20 at 15°, does not solidify when cooled to -15°, and gives an intense red coloration when dissolved in dilute hydrochloric acid and treated with potassium dichromate. The *hydrochloride* is a white crystalline powder, and melts at 167—168° with decomposition; a *platinochloride*, or *aurochloride* could not be obtained on account of the reducing property of the substance. The *hydrobromide* melts at 147°; the *hydriodide* at 131—132° with decomposition; and the *picrate* at 102° with decomposition. The *acetyl derivative*, $C_9H_{11}N_2Ac$, is an odourless, fluorescent oil which boils at 231—232° (110 mm.); and the *benzoyl derivative*, $C_9H_{11}N_2Bz$, melts at 79°. Both of the last-described compounds give red colorations with potassium dichromate and hydrochloric acid.

Benzylidenephenylpyrazolidine, $NH < \begin{matrix} NPh \cdot CH_2 \\ CH_2 \cdot C \cdot CHPh \end{matrix}$, obtained by heating phenylpyrazolidine with benzaldehyde at 150° in an atmosphere of carbonic anhydride, is an oil boiling at 280—290° (100 mm.).

Diphenylpyrazolidinesemicarbazide, $NHPh \cdot CO \cdot N < \begin{matrix} NPh \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix}$, is formed, with evolution of heat, when phenylpyrazolidine is treated with phenylcarbimide; it forms silky leaflets, and melts at 114°.

Diphenylpyrazolidinethiosemicarbazide, $NHPh \cdot CS \cdot N < \begin{matrix} NPh \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix}$, is prepared from phenylthiocarbimide and phenylpyrazolidine; it forms lustrous needles, and melts at 164—165°.

Phenylmethylpyrazolidine, $\text{NPh} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{NMe} \cdot \text{CH}_2 \end{smallmatrix}$, obtained by treating phenylpyrazolidine with methylic iodide and alcoholic alkali, is a yellow oil which boils at $175\text{--}180^\circ$ (90 mm.): it gives an intense red coloration in dilute solution with potassium dichromate and hydrochloric acid. Phenylbenzylpyrazolidine, $\text{CH}_2\text{Ph} \cdot \text{N} \begin{smallmatrix} \text{NPh} \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$, prepared from phenylpyrazolidine, benzyl chloride, and alcoholic alkali is a yellowish oil, boils at 225° (40 mm.), and gives in dilute solution with potassium dichromate and hydrochloric acid, a permanent blue coloration. A. R. L.

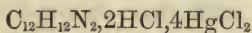
Pyrazines. By C. STOEHR (*J. pr. Chem.* [2], 48, 18—23; compare this vol., i, 486).—The author notices the chief points of difference between his previous paper and that of Wolff (this vol., i, 373) on this subject; to these attention has already been called (this vol., i, 486). To convince himself that Wolff's base is identical with his own, the author has prepared the salts described by Wolff from his own sample of the base; the results were practically identical with those obtained by Wolff. The paper concludes with a brief consideration of the probable manner in which the bonds in the pyrazine ring are disposed. A. G. B.

Synthesis of Pyrazine. By L. WOLFF (*Ber.*, 26, 1830—1833); compare Abstr., 1888, 809).—The gold salt previously obtained by the author from the products formed by heating acetalamine with oxalic acid (Abstr., 1888, 809) has now been proved to be a salt of pyrazine and to have the formula $\text{C}_4\text{H}_4\text{N}_2\text{AuCl}_3$. A yield of about 20 per cent. of the theoretical amount of the base may be obtained from acetalamine by adding 1 part of the latter to a concentrated warm solution of 3 parts of mercuric chloride, and then sufficient concentrated hydrochloric acid to dissolve the double salt which is precipitated. The liquid is then boiled for 10 minutes, filtered, rendered alkaline with anhydrous sodium carbonate, and distilled with steam. The distillate is acidified with hydrochloric acid, distilled to remove alcohol, &c., and the pyrazine then converted into the double salt with mercuric chloride, which is finally distilled with a very concentrated solution of potassium carbonate. The pure base is thus obtained as an oil which soon solidifies to white needles.

A. H.

Methyldipyridyls. By B. C. STOEHR and M. WAGNER (*J. pr. Chem.*, [2] 48, 1—16; compare Abstr., 1891, 80; 1892, 75).— $\beta\beta$ -Dimethyldipyridyl is prepared from β -methylpyridine by a method similar to that employed for making the $\alpha\alpha$ -derivative from α -methylpyridine (Abstr., 1891, 80). The portion which distils at $280\text{--}290^\circ$ crystallises, and is washed by ether free from alcohol. It is sparingly soluble in water and only slightly volatile with steam. It crystallises in small, lustrous tables or prisms, melts at 125° , and boils at 293° at the ordinary pressure, almost without decomposition. It is precipitated from its aqueous solution by alkalis, and is heavier

than water. Potassium ferrocyanide does not precipitate its solutions, but an orange-red ferrocyanide gradually separates when this reagent is added to them. It behaves as a diacid base. The *hydrochloride*, $C_{12}H_{12}N_2 \cdot 2HCl$, crystallises in slender, lustrous needles; it sublimes without melting. The *platinochloride*, $C_{12}H_{12}N_2 \cdot H_2PtCl_6$, crystallises in flat, reddish-yellow needles, or serrated laminæ. The *platinum salt*, $C_{12}H_{12}N_2 \cdot PtCl_4$, the *mercurochloride*,



(m. p. 221—222°), the *aurochloride*, $C_{12}H_{12}N_2 \cdot 2HAuCl_4$, the *argento-nitrate*, the *picrate*, $C_{12}H_{12}N_2 \cdot 2C_6H_3N_3O_7$, the *methiodide*, $C_{12}H_{12}N_2 \cdot 2MeI$, with its *cadmioidide*, $C_{12}H_{12}N_2 \cdot 2MeI \cdot CdI_2$, and the *methochloride*, $C_{12}H_{12}N_2 \cdot 2MeCl$, with its *platinochloride*, $C_{12}H_{12}N_2 \cdot 2MeCl \cdot PtCl_4$, and its *mercurochloride*, $C_{12}H_{12}N_2 \cdot 2MeCl \cdot 4HgCl_2$ (m. p. 148—149°) are described.

Dipyridyl-ββ-dicarboxylic acid, $C_{10}H_6N_2(COOH)_2$, is the product of the oxidation of ββ-dimethyldipyridyl by potassium permanganate at the temperature of the water-bath; it crystallises in small, lustrous prisms (with 2 mols. H_2O), and is more soluble in water than is the αα-acid (Abstr., 1892, 75) but dissolves very sparingly in ether, alcohol, chloroform, and benzene. It is not coloured by ferrous sulphate, and may be heated at 280° without apparent change. The *ammonium salt* is very soluble in water, the *calcium salt* crystallises well, the *copper*, *silver*, *lead*, *mercury*, *cobalt*, and *nickel salts* are more or less insoluble, amorphous precipitates.

When the acid is heated with glacial acetic acid at 300°, the carboxyl groups are eliminated and a salt of γγ-dipyridyl is obtained. This proves the dimethyl-derivative to be a γγ-dipyridyl compound.

ββ-Dimethyl-γγ-dipiperidyl, $C_{12}H_{24}N_2$, is prepared by acting on ββ-dimethyl-γγ-dipyridyl with nascent hydrogen from sodium and water, and is purified by taking advantage of the insolubility of its hydrochloride in alcohol. It is a colourless, viscid oil, boils at 299—300° (corr.), and gradually crystallises; it is unusually soluble in water, with an alkaline reaction, and is also soluble in alcohol and ether; it has a bitter taste and a narcotic odour. The *hydrochloride*, $C_{12}H_{24}N_2 \cdot 2HCl$, crystallises in dazzling white needles, and is unchanged at 290°. The *platinochloride*, $C_{12}H_{24}N_2 \cdot H_2PtCl_6 + 2\frac{1}{2}H_2O$, crystallises in reddish-yellow laminæ, darkens at 250°, and melts at 256—258°. The *mercurochloride*, $C_{12}H_{24}N_2 \cdot 2HCl \cdot 4HgCl_2$ (m. p. 210—211°), the *cadmioidide*, $C_{12}H_{24}N_2 \cdot 2HI \cdot CdI_2$ (m. p. 270—272°), and the *nitrosamine* are described.

A. G. B.

Relation of Safranines to Indulines. By O. FISCHER and E. HEPP (*Ber.*, 26, 1655—1657; see also *Ber.*, 26, 1194).—When phenosafranine is diazotised in alcoholic solution in the presence of hydrochloric acid, the hydrochloride of a compound which the authors name *aposafranine* is obtained. If the salt is heated with $2\frac{1}{2}$ times its weight of aniline in the water bath, until the product dissolves in concentrated sulphuric acid with a reddish-violet coloration, it is converted into the hydrochloride of the induline, $C_{16}H_{13}N_3$. The latter crystallises in beautiful, lustrous, green prisms,

and gives a reddish-violet solution with concentrated and dilute mineral acids. When heated with dilute sulphuric acid under pressure, it yields benzolindone hydrate (*Annalen*, **266**, 253). It is, therefore, the simplest induline, $\text{NH}:\text{C}_6\text{H}_3\begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}\text{Ph} > \text{C}_6\text{H}_4$. When heated with aniline at 140–150°, it is converted into phenylinduline (m. p. 231°), which is identical with the compound obtained from azophenine, and with that obtained from the amidophenylinduline of the amidobenzene melt. Hence the authors conclude that in the preparation of induline from amidoazobenzene, a safranine is formed as an intermediate compound. E. C. R.

Alkaloids of *Gelsemium sempervirens*. By A. R. CUSHNY (*Ber.*, **26**, 1725–1727).—The following two have been isolated:—

Gelsemine [Eng. “Gelsemin (Gerrard)”]; Ger. “Krystallisirtes Gelseminin”] is white, amorphous, bitter, and strongly alkaline; its salts are crystalline. Sulphuric acid and manganese dioxide or potassium dichromate give a red coloration, changing gradually to green. In the frog it causes tetanic convulsions, and finally deadening of the sensory nerve-endings; on rabbits it has no effect. The *hydrochloride* is $\text{C}_{49}\text{H}_{63}\text{N}_5\text{O}_{14}\cdot 2\text{HCl}$.

Gelseminine (Ger. “Gelseminin amorph.”) is colourless, amorphous, strongly alkaline; the salts are amorphous. Sulphuric acid and oxidising agents give a violet coloration, changing to green. It is very poisonous, producing respiratory failure in rabbits as well as in frogs; it also causes dilatation of the pupil. The *platinochloride* is stated to have the formula $\text{C}_{42}\text{H}_{47}\text{N}_3\text{O}_{14}\cdot \text{HCl}\cdot \text{PtCl}_4$ (!). C. F. B.

Ptomaine from the Urine in Cases of Eczema. By A. B. GRIFFITHS (*Compt. rend.*, **116**, 1205–1206).—The urine of patients suffering from eczema yields a ptomaine, $\text{C}_7\text{H}_{15}\text{NO}$, which is not obtained from normal urine. It is a white, crystalline compound, soluble in water, and having a feebly alkaline reaction. It yields a crystalline hydrochloride, aurochloride, and platinochloride. With phosphotungstic acid, its solutions yield a brownish precipitate; with phosphomolybdic acid, a yellowish precipitate; with picric acid, a yellow precipitate; with silver nitrate, a yellowish precipitate; with mercuric chloride, a greenish precipitate, and a precipitate also with Nessler's reagent.

The base is poisonous, and when injected under the skin of a rabbit produces local inflammation with high fever, resulting in death. C. H. B.

Chitins. By N. P. KRAWKOW (*Zeit. Biol.*, **29**, 177–198).—From the examination of the chitinous skeleton of various invertebrates, the following conclusions are drawn:—

1. There are various kinds of chitin, differing from one another in the reaction they give with iodine.
2. Chitins are amido-derivatives of carbohydrates.
3. The carbohydrate derivatives give reactions with iodine very similar to those of the chitins from which they are obtained.

4. The different kinds of chitins may assist in the zoological classification of the animals which yield them.

5. Chitin resembles the pathological substance amyloid in its behaviour to iodine and aniline dyes.

6. The occurrence of cellulose in animals is only proved in the case of the Tunicates. In Arthropods and Cephalopods its presence appears to be in the highest degree doubtful.

7. In chitinous tissues, chitin is in loose chemical combination with proteid material. W. D. H.

δ -Achroglobulin from the Blood of certain Mollusca. By A. B. GRIFFITHS (*Compt. rend.*, **116**, 1206—1207).— δ -Achroglobulin is obtained from the blood of certain species of *Doris*, and exists in a reduced and in an oxidised condition. It has the composition $C_{659}H_{792}N_{165}SO_{153}$, and 100 grams absorb 125 c.c. of oxygen at normal temperature and pressure. A solution in a dilute magnesium sulphate solution has the specific rotatory power $[\alpha]_D = -54^\circ$.

δ -Achroglobulin yields with methane a yellowish compound, with acetylene a greenish compound, and with ethylene a brownish compound, and each of them dissociates in a vacuum. C. H. B.

Proteid Reactions. By J. W. PICKERING (*J. physiol.*, **14**, 347—382).—Cobalt salts and potash give distinctive colour reactions with proteids, proteoses, and peptones. Native proteids give a heliotrope purple; proteoses and peptone a red-brown. Certain albuminoids (gelatin, mucin, keratin elastin, &c.) and various organic substances related to proteids (biuret, alloxan, uric acid xanthine, hypoxanthine, &c.), give similar colours.

Gelatin gives a play of colours in spectral order; so also do alloxan, biuret, and allantoin.

It is regarded as probable that these reactions, like those similarly produced with copper salts (the so-called biuret reaction) and nickel salts (Gnezda), are due to the presence of the group CONH, and not to cyanogen, as Gnezda considered; the difference between a native proteid and a peptone being one in the atomic arrangement of the group.

When a cobalt salt has entered into the proteid molecule, it can be easily displaced by a nickel salt, and that in turn by a copper salt, each in turn yielding its characteristic colour reaction.

The precipitates of proteid produced by mercuric chloride, silver nitrate, salicylsulphonic, phosphotungstic, and phosphomolybdic acids yield typical proteid colour reactions. The nucleo-albumins behave as ordinary proteids, not as peptones, in their colour reactions.

The xanthoproteic reaction and Millon's reaction probably are due to a hydroxybenzene nucleus in the proteid molecule. The reactions of Liebermann and Adamkiewicz depend on the aromatic portion of the proteid molecule. Krasser's reaction (a brilliant red with solution of alloxan) probably depends on an amido-group, as stated by Krasser himself.

When metamidobenzoic acid is heated with phosphorus pentachloride, it yields a substance which behaves as Grimaux stated, very

like a proteid, coagulating with heat, especially in presence of a calcium salt. The evidence that Grimaux advanced that this "colloïde amidobenzoïque" is free from calcium phosphate is not regarded as satisfactory. It is, however, to be noted that this material gives, with alkaline solutions of copper, nickel, and cobalt, reactions like those of a proteid.

No evidence was found that Fröhde's reaction (blue precipitate when a solid proteid is heated with sulphuric and molybdic acids) and Axenfeld's reaction (blue appearance when a proteid is heated with auric chloride and formic acid, gas being given off) are due to any special molecular group. In connection with the last-named reaction, it was found that if the heating is continued for five minutes at the boiling point, the auric chloride is reduced, and a mirror of gold lines the test-tube.

W. D. H.

Hæmoglobin which contains Phosphorus. By Y. INOKO (*Zeit. physiol. Chem.*, **18**, 57—60).—Hoppe-Seyler and, later, Jaquet showed that the blood crystals from birds contain phosphorus. This has been explained by the existence of a nucleus in their blood corpuscles. The present investigation relates to (1) whether nucleic acid can be obtained from birds' blood crystals, and (2) whether an analogous crystalline compound can be obtained by adding nucleic acid to the oxyhæmoglobin of mammals' blood. The answer to the first question is almost certainly in the affirmative, as adenine was prepared from the crystals. With regard to the second point, oxyhæmoglobin from horses' blood was dissolved in a solution of nucleic acid, and cooled to 0°, when a substance crystallised out in prisms which contained 0.4 per cent. of phosphorus, that is, approximately the same as in the blood crystals of the goose.

W. D. H.

Dissociation of Oxyhæmoglobin in Aqueous Solution. By G. HÜFNER (*Zeit. physikal. Chem.*, **11**, 794—804).—The author shows that for solutions of oxyhæmoglobin varying in concentration from 10 to 17.5 grams per litre, the extinction-coefficient is proportional to the concentration, and attributes the discrepancy between his results and those of van Noorden (*Zeit. physiol. Chem.*, **4**, 23) to the different photometric methods employed. There is, therefore, probably no decomposition of large molecular aggregates into smaller as the dilution increases. There is, however, in all solutions a dissociation of oxyhæmoglobin into free oxygen and hæmoglobin. The author endeavoured to show this by a change of colour in a solution of hæmoglobin, separated from a solution of oxyhæmoglobin by a membrane of vegetable parchment, which allows oxygen and water to pass through it, but is impermeable to the other substances. No definite result was obtained, probably owing to the destruction of the oxygen by a reducing substance before it could pass through the membrane.

J. W.

Organic Chemistry.

Formation of Hydrocyanic acid by the Action of Nitric acid on Sugar, &c. By F. B. BURLS, R. E. EVANS, and C. H. DESCH (*Chem. News*, 68, 75).—The authors find that hydrocyanic acid is formed during the action of nitric or nitrous acid on sugar, caramel, or finely divided charcoal. D. A. L.

Pentaglycerol. By H. HOSAEUS (*Annalen*, 276, 75—79).—Pentaglycerol, $\text{CMe}(\text{CH}_2\cdot\text{OH})_3$, is obtained by the action of formaldehyde (3 mols.) on propaldehyde (1 mol.) in presence of water and calcium hydroxide; it crystallises from alcohol in white needles, melts at 199° , sublimes without decomposition, and is very easily soluble in water. The *triacetyl* derivative, $\text{C}_5\text{H}_9(\text{OAc})_3$, is a colourless liquid, and the *tribenzoyl* derivative, $\text{C}_5\text{H}_9(\text{OBz})_3$, forms colourless needles. When pentaglycerol is heated in a reflux apparatus with potassium dichromate and sulphuric acid, formic and acetic acids are produced. A. R. L.

Penterythritol. By P. RAVE and B. TOLLENS (*Annalen*, 276, 58—69).—Among the bye-products obtained in the preparation of penterythritol, $\text{C}(\text{CH}_2\cdot\text{OH})_4$ (Abstr., 1892, 128), a compound has been isolated which is more soluble in water than penterythritol, and melts at $174\text{--}190^\circ$; it gave values on analysis indicating that it may be a "*tetraglycerol*," $\text{CH}(\text{CH}_2\cdot\text{OH})_3$. The volatile bye-products consist of an aldehyde, recognised by the magenta sulphurous acid reaction, together with formic and acetic acids.

Tetrabenzoylpenterythritol, $\text{C}_5\text{H}_8(\text{OBz})_4$, prepared by the Baumann-Schotten method crystallises in long needles, and melts at $99\text{--}101^\circ$. When penterythritol is heated for four hours at 100° with phosphorus tribromide (8 parts) and subsequently at 150° , the product extracted with cold alcohol, and the residue boiled with alcohol and filtered from phosphorus, the *tetrabromhydrin*, $\text{C}_5\text{H}_8\text{Br}_4$, separates from the filtrate in colourless leaflets; it melts at $154\text{--}156^\circ$. The *tribromhydrin*, $\text{C}_5\text{H}_8\text{Br}_3\cdot\text{OH}$, is obtained from the cold alcoholic extract; it is also produced by heating penterythritol with phosphorus tribromide at a temperature not higher than 100° ; it melts at 60° .

When penterythritol is oxidised with nitric acid of 1.4 sp. gr., oxalic and glycollic acids are obtained, but if dilute nitric acid in the cold is employed, *diglycollaldehyde*, $\text{CHO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CHO}$, is obtained. The latter forms a *hydrazone*, $\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}$, melting at 108° .

When penterythritol tribromhydrin is treated with zinc dust and acetic acid, an unsaturated alcohol, $\text{C}_5\text{H}_8\cdot\text{OH}$, is obtained, boiling at $120\text{--}128^\circ$; it does not solidify when cooled to -30° . A similar compound is formed by acting with zinc dust and acetic acid on penterythritol triiodhydrin. A. R. L.

Carbohydrates of the Jerusalem Artichoke. By C. TANRET (*Compt. rend.*, 117, 50—53).—The juice of Jerusalem artichokes, after
VOL. LXIV. i. 2 x

treatment with basic lead acetate and removal of the lead, is mixed with barium hydroxide and fractionally precipitated with alcohol, the process of fractionation being repeated on the products.

Two carbohydrates, much more soluble in alcohol than inulin, pseudoinulin, or inulenin, are thus obtained.

Helianthenin crystallises in microscopic needles which melt at 176° . When dried at 110° , it has the composition $12C_6H_{10}O_5 + 3H_2O$. It is soluble in its own weight of water, and is also very soluble in dilute alcohol, but the solubility diminishes rapidly as the concentration of the alcohol increases. Its rotatory power is $[\alpha]_D = -23.5^{\circ}$, but under the influence of dilute acids this increases to -70.2° . *Helianthenin* is fermented by beer yeast with some difficulty under ordinary conditions.

Synanthrin, which when dried at 110° has the composition $8C_6H_{10}O_5 + H_2O$, is amorphous and almost tasteless. It melts at 170° , dissolves in all proportions in water or dilute alcohol, and in 10 parts of alcohol of 84° . Its rotatory power is $[\alpha]_D = -17^{\circ}$, and when treated with dilute acids this rises to -70.6° owing to the formation of glucose and levulose. *Synanthrin* is fermentable. It has the peculiar property of preventing the formation of barium saccharate, which only forms when at least 1.5 parts of saccharose is present for 1 part of *synanthrin*. The inactive sugar said to be obtained from artichokes and described as levulin or *synanthrose* is a mixture of saccharose and *synanthrin*.

Helianthenin and *synanthrin* also occur in the dahlia and in elecampane.

C. H. B.

Lime Tree Honey. By MAQUENNE (*Compt. rend.*, 117, 127—129). The fresh leaves of the lime tree, when treated simply with water and evaporated on a water bath to a syrupy consistence, yield about 1 per cent. of a very sweet, brown syrup with a bitter after-taste. If this is treated with alcohol of 90° , a gummy substance is precipitated, and the liquid deposits microscopic crystals which do not consist of saccharose. After purification by repeated crystallisation from alcohol, the crystals are identical with the melezitose obtained from Persian manna. Its rotatory power is $+88.8^{\circ}$, and is reduced to about 50° after complete hydrolysis; when boiled with phenylhydrazine acetate, it yields ordinary well crystallised phenylglucosazone and gelatinous *phenylturanosazone*, which is characteristic of the biose formed in the feeble hydrolysis of melezitose; it melts at the same temperature as melezitose from manna, and its solutions crystallise when a fragment of melezitose is introduced, but are not affected by other sugars.

The leaves contain a reducing sugar which seems to be ordinary glucose, and also a gummy substance. Approximately, 40 per cent. of the crude "lime tree honey" is melezitose.

C. H. B.

Preparation of Glycogen from the Liver and Muscles. By V. KISTYAKOFFSKY (*J. Russ. Chem. Soc.*, 25, 60—73).—Liver and muscle are taken from the animal immediately after death, and, to prevent fermentation, rubbed up at once in an iron mortar cooled to

a very low temperature. The homogeneous mass is then extracted with a cooled 1—2 per cent. solution of hydrochloric acid until the last extracts cease to give the glycogen reaction with iodine. When it is not desired to effect a complete extraction of the glycogen, acid of 0·2 to 0·7 per cent. strength may be used. The solution thus obtained is coloured by hæmoglobin, and contains albuminous matter, which is precipitated by means of mercuric iodide; this precipitate is filtered off and washed on the filter with dilute mercuric iodide solution until it is free from glycogen. The glycogen is precipitated from the filtrate and washings by the addition of alcohol (about 1·5 volumes), collected on a filter, and washed, first with 75 per cent. alcohol, and then with 95 per cent. alcohol and ether. When dried over sulphuric acid, the glycogen forms a light, amorphous, snow-white powder, containing no nitrogenous admixture, and leaving only traces of ash. Dried in the air, the glycogen is obtained in the form of a resinous mass difficult to powder. This method of cold extraction may be employed for the quantitative estimation of glycogen in animal tissues, the results obtained being somewhat lower than those arrived at by Brücke's method.

J. W.

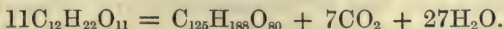
Specific Rotatory Power of Glycogen. By HUPPERT (*Zeit. physiol. Chem.*, **18**, 137—143).—The specific rotatory power of glycogen is variously given by different observers. In the present investigation, the following formula was used,

$$[\alpha]_D = \frac{\alpha}{\alpha'} \frac{12}{11} 52\cdot5^\circ,$$

α being the rotation observed in the glycogen solution, α' that in the dextrose solution formed by hydrolysis from it, the tubes being of the same length. 52·5 is the specific rotatory power of dextrose, and the ratio 12:11 is obtained by taking the formula of glycogen as $6C_6H_{10}O_5 + H_2O$, so that 11 parts of glycogen yield 12 of dextrose. The average of five experiments gave $[\alpha]_D = +196\cdot63^\circ$ as the specific rotatory power of glycogen. Erythrodextrin gives the same colour with iodine as glycogen, and the spectroscopic appearances are identical. The specific rotatory power of erythrodextrin, estimated in the same way, is $+196\cdot5^\circ$, so that the polarimeter is of no use in distinguishing between the two substances.

W. D. H.

Cryoscopy, &c., of Caramel. By A. SABANÉEFF and I. ANTUSHEVITCH (*J. Russ. Chem. Soc.*, **25**, 23—31).—Dialysed caramel, prepared by repeated precipitation from its aqueous solution by alcohol, is not a carbohydrate, carbonic anhydride being given off on its formation from sugar. From determinations of its molecular weight (nearly 3000) in aqueous solution, and combustions of the substance itself, as well as analysis of the barium derivative, the author proposes the approximate formula $C_{125}H_{188}O_{80}$. The formation from sugar would then be represented by the equation



The aqueous solution of dialysed caramel is affected by heat and by

the action of light, the depression of the freezing point increasing, probably in consequence of a process of hydration, and formation of substances with lower molecular weight. Caramel in aqueous solution is capable of undergoing a species of fermentation, in virtue of which the depression is diminished. This is a process of dehydration with formation of products of much greater molecular weight.

Gélis' caramel is dialysed caramel whose solutions have undergone change by heating, whilst Graham's mucilaginous caramel, which diffused more slowly than albumen, is the product of the specific fermentation mentioned above. J. W.

Decomposition of Ethers by Hydrogen Haloïds. By W. LIPPERT (*Annalen*, 276, 148—199).—These experiments were made in order to determine the extent to which the decomposition by hydrogen haloïds of compounds consisting of two or more organic radicles and oxygen is affected by the constitution of the compounds and the constitution of their radicles.

The ethers (5—10 grams) were introduced into tubes sealed at one end, and saturated at 0° with the hydrogen haloid; the open ends of the tubes were then sealed, and they were heated at 100°.

The ethers were prepared by Williamson's method, namely, acting on the alkyl haloïds with the sodium or potassium alkyloxides; the alkyloxides prepared from the secondary and also from the higher primary alcohols must be free from an excess of the alcohol. The dissolution of sodium in the primary alcohols takes place more readily than in the secondary and tertiary alcohols. Attempts to combine trimethylcarbinyl iodide with pyridine were unsuccessful, although the isomeric butylic iodides combine with it readily to form crystalline compounds.

The vapour densities of the dialkylethylene ethers were determined in a Gay Lussac-Hofmann apparatus as modified by Lothar Meyer, so that the vapour tensions could be determined with one and the same quantity of substance at different temperatures, and under pressures varying from a few millimetres of mercury up to 2 atmospheres. The vapour tensions observed between 10° and 100° are represented by curves, from an inspection of which it is evident that the vapour tensions of the dialkylethylene ethers vary inversely as the number of carbon atoms in their molecules.

The general results are in harmony with Silva's rule in the following modified form. When a mixed ether is decomposed by a hydrogen haloid, the halogen combines with the radicle of lower equivalent. In the case of bi- and ter-valent ethers, the halogen generally combines with the univalent radicles. The smaller the number of carbon atoms contained in its radicles, the easier the decomposition of an ether.

When hydrogen iodide acts on a mixed ether containing isomeric radicles, the halogen combines with the normal hydrocarbon radicle. When both radicles are derived from the same hydrocarbon, the halogen combines with that of primary structure. Propyl isopropyl ether forms an exception to this rule, as in this case the halogen combines with the isopropyl group.

The action of hydrogen iodide is in all cases more energetic than that of hydrogen bromide.

The results are tabulated below.

a. Univalent Ethers.

Ethers.	Haloïds.	Hydroxides.
$\text{CHMe}_2 \cdot \text{O} \cdot \text{Et}$	EtI	$\text{CHMe}_2 \cdot \text{OH}$
$\text{CH}_2 \cdot \text{CHMe}_2 \cdot \text{O} \cdot \text{Et}$	EtI	$\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{OH}$
$\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{Pra}$	$\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \text{I}$	$\text{Pra} \cdot \text{OH}$
$\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CHMe}_2$	$\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \text{I}$	$\text{CHMe}_2 \cdot \text{OH}$

b. Univalent Ethers with Isomeric Radicles.

Ethers.	Haloïds.	Hydroxides.
$\text{CHMe}_2 \cdot \text{O} \cdot \text{Pra}$	$\text{CHMe}_2 \text{I}$	$\text{Pra} \cdot \text{OH}$
$\text{CH}_2 \text{Me} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CHMe}_2$..	$\text{CH}_2 \text{Me} \cdot \text{CH}_2 \cdot \text{CH}_2 \text{I}$	$\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{OH}$
$\text{CH}_2 \text{Me} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CHMeEt}$	$\text{CH}_2 \text{Me} \cdot \text{CH}_2 \cdot \text{CH}_2 \text{I}$	$\text{CHMeEt} \cdot \text{OH}$
$\text{CHMeEt} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CHMe}_2$	CHMeEtI	$\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{OH}$

c. Bivalent Ethers.

Ethers.	Haloïds.	Hydroxides.
$\text{CH}_2(\text{OMe})_2$	2MeI	HCOH
$\text{CH}_2(\text{OEt})_2$	2EtI	HCOH
$\text{CH}_2(\text{OPra})_2$	2PraI	HCOH
$\text{CH}_2(\text{OC}_5\text{H}_{11})_2$	$2\text{C}_5\text{H}_{11}\text{I}$	HCOH
$\text{CHMe}(\text{OEt})_2$	2EtI	MeCOH
$\text{C}_2\text{H}_4(\text{OMe})_2$	2MeI	$\text{C}_2\text{H}_4(\text{OH})_2$
$\text{C}_2\text{H}_4(\text{OEt})_2$	2EtI	$\text{C}_2\text{H}_4(\text{OH})_2$
$\text{C}_2\text{H}_4(\text{OPra})_2$	2PraI	$\text{C}_2\text{H}_4(\text{OH})_2$
$\text{C}_2\text{H}_4(\text{OC}_4\text{H}_9)_2$	$2\text{C}_4\text{H}_9\text{I}$	$\text{C}_2\text{H}_4(\text{OH})_2$

d. Tervalent Ethers.

Ethers.	Haloïds.	Hydroxides.
$\text{CH}(\text{OEt})_3$	3EtI	HCOOH
$\text{CH}(\text{OPra})_3$	3PraI	HCOOH
$\text{C}_3\text{H}_5(\text{OEt})_3$	3EtI	$\text{C}_3\text{H}_5(\text{OH})_3$

Zinc Isopropide. By V. RAGOZIN (*J. Russ. Chem. Soc.*, **24**, 549—552).—Isopropyl iodide (170 grams), mixed with absolute ether (100 grams), is heated to boiling on the water bath with granulated zinc (100 grams) and powdered zinc sodium (2—3 grams). The reaction is complete in nine hours, and the contents of the flask are then distilled in a current of dry carbonic anhydride, first from the water bath and afterwards from an oil bath. The higher boiling portion, on redistillation, gives a fraction boiling at 135—137°, which consists of nearly pure zinc isopropide. The yield is about 20 per cent. of that theoretically possible.

Zinc isopropide cannot be prepared in the pure state, as it decomposes more or less on distillation, even under reduced pressure. Under a pressure of 40 mm. it boils between 94° and 98°. It is a clear, colourless liquid, which fumes strongly in the air, but may be transferred from one vessel to another without igniting. When spread over a large surface, however, it inflames spontaneously. Exposed to the slow action of air in a closed vessel, it absorbs oxygen with formation of zinc isopropoxide, $\text{Zn}(\text{OPr}^a)_2$, which separates in prismatic crystals.

J. W.

Alkyl Compounds of Magnesium. By H. FLECK (*Annalen*, **276**, 129—147).—A continuation of Löhr's experiments (*Abstr.*, 1891, 682). Magnesium amalgam acts on ethylic iodide with development of heat when the two are brought together in an exhausted sealed tube, but to complete the reaction it is necessary to heat the tubes at 100°, magnesium diethide and gaseous products being formed. Aluminium amalgam has no action on ethylic iodide at the ordinary temperature, but when the two are heated at 130°, gaseous products, and much mercuric and aluminium iodides are obtained, together with a liquid containing aluminium. An alloy of zinc and magnesium acts on ethylic iodide at 120°, forming a little magnesium diethide and a large amount of metallic iodides. Magnesium-cadmium alloy acts on ethylic iodide at 120°, forming normal butane and other hydrocarbons, together with metallic iodides. Magnesium diethide, prepared by Löhr's method, reacts with water, forming ethane and magnesium iodide.

Trimethylcarbinol is obtained by the action of acetic chloride on magnesium dimethide, and the same compound is formed from acetic chloride and magnesium diethide, but certain hydrocarbons are simultaneously produced.

Magnesium diphenyl is prepared by heating mercury diphenyl with an excess of magnesium powder in an exhausted sealed tube at 200—210° for 5—6 hours. The tube is opened under benzene, heated on the water bath with some of this solvent, which dissolves the excess of mercury diphenyl, after which the magnesium diphenyl is extracted with a mixture of ether and benzene, and the solution evaporated in an atmosphere of dry nitrogen; it is a light grey substance, insoluble in carbon bisulphide, ether, and benzene, although it dissolves freely in a mixture of the last two. With water, it gives magnesium hydroxide and benzene. It burns in air, forming magnesium oxide and a carbonaceous mass, but when a

current of dry air is passed into anhydrous benzene containing magnesium diphenyl in suspension, slow oxidation takes place, and at the end of three months the compound is converted into magnesium diphenoxide, $\text{Mg}(\text{OPh})_2$. When bromine is slowly dropped on to magnesium diphenyl covered with a layer of anhydrous ether, it yields magnesium bromide and bromobenzene. If magnesium diphenyl is heated above 210° in a sealed tube, a tar-like mass is formed from which diphenyl may be isolated. Benzal chloride reacts with magnesium diphenyl, forming triphenylmethane, whilst phosphorus trichloride gives rise to diphenyl phosphorus chloride, PClPh_2 (Michaelis, 1875).

It is interesting to note that compounds such as magnesium alkyl iodides do not seem to exist; in the case of zinc and mercury these are the initial products of the action of the metals on the alkyl iodides, and they subsequently decompose, yielding metallic alkyls and iodides. The magnesium compounds are more active than the analogous zinc compounds.

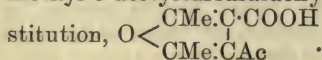
A. R. L.

Action of Acetylacetone on Bromacetone in presence of Sodium Ethoxide. By G. MAGNANINI (*Gazzetta*, 23, i, 462—469).

—Bromacetone is added to an alcoholic solution of sodium ethoxide and acetylacetone, the reaction completed by heating on the water-bath, and the product distilled in a current of steam; the residue is a heavy, red oil, which could not be purified, and decomposes on distillation. It seems to be *unsymmetrical triacetylcane*, $\text{CHAc}_2\cdot\text{CH}_2\text{Ac}$, and by heating either it, or the products obtained by its direct distillation, with ammonia in a sealed tube at 180° , 2:5-dimethyl-3-

acetylpyrroline, $\begin{array}{c} \text{CAc}:\text{CMe} \\ | \\ \text{CH}:\text{CMe} \end{array} > \text{NH}$, is obtained. This compound is identical with the substance of the composition, $\text{C}_8\text{H}_{11}\text{NO}$, obtained by Magnanini and Scheidt (*Abstr.*, 1892, 1429) by heating dehydrodiacetyllevulinic acid with ammonia; it is a feeble base, melts at 94° , and gives a *hydrochloride*, $\text{C}_8\text{H}_{11}\text{NO}\cdot\text{HCl}$, which is decomposed by water, and forms whitish needles which decompose at above 150° . The constitution of the base is established by the fact that it gives 2:5-dimethyl-3-cinnamalpyrroline when boiled with benzaldehyde and potash.

Dehydrodiacetyllevulinic acid is, therefore, a derivative of 2:5-dimethyl-3-acetylfurfuraldehyde, and probably has the following constitution,



W. J. P.

Flowers of *Tagetes glandulifera*. By O. HESSE (*Annalen*, 276, 87—88).—*Tagetes glandulifera* is a plant of the order Compositæ, met with in Argentina, where the flowers are used as a stomachic, aperient, diuretic, and diaphoretic, and are employed in cases of gastritis and indigestion. Their application is, however, said to be attended with danger.

The author finds that the flowers do not contain any alkaloid which can be extracted with ether or chloroform. Light petroleum, however, extracts a substance which, when crystallised from alcohol,

melts at 62° ; it may be cerylic acetate, as the alcohol obtained on hydrolysis agreed in properties with cerylic alcohol, and the original substance was regenerated by treating the alcohol with acetic anhydride; no analyses or other data are given.

A. R. L.

Thermochemistry of Chloracetic acid. By S. TANATAR (*J. Russ. Chem. Soc.*, **24**, 694—698).—The unstable modification of chloracetic acid (m. p. 52°) changes into the stable modification (m. p. 63°) with development of heat = 0.65 Cal. per gram-molecule. The heat of dissolution of the stable acid was found to be -3.47 Cal., and that of the unstable acid -2.77 Cal., giving a difference of 0.70 Cal., nearly equal to the heat of transformation directly observed. Both acids show a normal molecule in aqueous solution, and a double molecule in benzene solution.

J. W.

Decomposition of Chloracetates and Bromacetates. By J. H. KASTLE and B. C. KEISER (*Amer. Chem. J.*, **15**, 471—493).—The salts used in these experiments were the potassium, sodium, ammonium, magnesium, calcium, and strontium chloracetates, and sodium bromacetate. A weighed quantity of the salt was heated with water, and the amount of decomposition determined at stated intervals of time by titration of the liberated glycollic acid with N/10 potash solution. The following conclusions are drawn from the experiments. (1.) The decomposition is greatly retarded by increasing the quantity of water. (2.) The decomposition is non-reversible, and can be carried to completion. (3.) The decomposition, at certain stages of dilution, probably at all, is independent of the nature of the base in the salt. (4.) The coefficients of velocity of the decomposition at N, N/3, and N/10 dilutions are inversely proportional to the coefficients of affinity of chloracetic and bromacetic acids at these dilutions. (5.) The decomposition reaches a minimum at a dilution somewhat above N/10, from which point to a dilution of 1,000 litres the decomposition is nearly constant. (6.) The velocity of decomposition is slightly accelerated by glycollic acid proportionately to the quantity of acid present. Other acids, feebler than chloracetic acid, have also been found to *accelerate* the decomposition in the order of their affinities. Acids stronger than chloracetic acid have the reverse effect. (7.) The velocity is also slightly accelerated by potassium chloride.

The views which the authors hold with regard to the reason for the decrease of velocity in the decomposition of these salts have already been set forth in the discussion on the decomposition of silver chloracetate (this vol., ii, 266). Ostwald (*Zeit. physikal. Chem.*, **11**, 431) has questioned the validity of the explanation there proffered; the authors fail, however, to discover any essential difference between their views and those of Ostwald on the subject.

It is noted in the experimental part of the paper, that when sodium bromacetate is heated with a small quantity of water, a little glycollide is always formed, and subsequently dissolves as glycollic acid. It would thus seem that in the decomposition of these salts by water, there is a secondary reaction to be taken into account.

A. G. B.

Thermochemistry of β -Dibromopropionic acid. By S. TANATAR (*J. Russ. Chem. Soc.*, **24**, 615—620).—The modification of β -dibromopropionic acid melting at 51° evolves about 0.5 Cal. for a molecular proportion on passing into the modification melting at 63° . The heat of dissolution of the (? higher melting) acid is 4.0 Cal. at 13° , and the heat of neutralisation of a decinormal solution with decinormal potash is 15.4 Cal., a value much higher than that usually observed in the case of organic acids. The action of a decinormal solution of hydrochloric acid on an equivalent solution of potassium β -dibromopropionate is accompanied by the absorption of 0.96 Cal., whilst the opposite reaction was found to develop heat = 0.71 Cal.

Decinormal solutions of the acid and sodium acetate react with development of heat = 1.9 Cal. Solutions of the free acid and its potassium salt may be mixed without thermal effect. The potassium salt (1 mol.) is further acted on by potash (1 mol.) in decinormal solution, with development of heat = 13.4 Cal. and formation of potassium bromide.

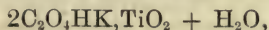
J. W.

Ethereal Oil from the Root of *Aspidium filix mas*. By A. EHRENBURG (*Arch. Pharm.*, **231**, 345—356).—The ethereal extract of the root of *Aspidium filix mas*—"oleum æthereum filicis"—is shown to owe its property as a cure for worms not to the filicic acid contained in it, but to the ethereal oil. The oil is obtained by steam distillation of the freshly-gathered air-dried roots, which yield in April, June, and September to November respectively, 0.008, 0.025, and 0.04—0.045 per cent. of ethereal oil. This oil contains 40 per cent. of free acids, chiefly of the fatty series from propionic to capric; butyric acid was, however, the only one that could be identified with certainty. The rest of the oil was hydrolysed by heating it with alcoholic potash; among the products were hexyl and octyl alcohols, and probably some aromatic alcohol, perhaps belonging to the series of terpenes; and, besides these, acids of the fatty series from butyric to pelargonic, amongst which again butyric acid alone could be identified with certainty.

C. F. B.

Combination of Oxalic acid with Titanic and Stannic acids.

By E. PÉCHARD (*Compt. rend.*, **116**, 1513—1516).—Titanic acid, prepared by the action of sodium carbonate on a solution of titanium chloride, dissolves readily in a warm solution of potassium hydrogen oxalate, and when the liquid cools, *potassium oxalotitanate*,



separates in colourless crystals which seem to belong to the triclinic system. It can be recrystallised from warm water, but is insoluble in alcohol, which precipitates it from aqueous solutions in slender, colourless needles. The salt is decomposed by alkalis, but the precipitation of the titanic acid is not complete. *Barium oxalotitanate*, $(\text{C}_2\text{O}_4\text{H})_2\text{Ba}, \text{TiO}_2 + \text{H}_2\text{O}$, is obtained as a white, crystalline precipitate by the addition of a solution of barium chloride to a solution of the preceding salt. If a solution of the barium salt is exactly decomposed by sulphuric acid, and the liquid is allowed to evaporate in a vacuum,

oxalotitanic acid, $2\text{C}_2\text{O}_4\text{H}_2\text{TiO}_2 + 2\text{H}_2\text{O}$, separates in acicular crystals, which effloresce rapidly and are insoluble in water or alcohol; the solution of this compound is strongly acid, but it does not combine readily with alkalis.

Gelatinous stannic acid likewise dissolves readily in a solution of potassium hydrogen oxalate, and on evaporation *potassium oxalostannate*, $2\text{C}_2\text{O}_4\text{HK}, \text{SnO}_2 + 5\text{H}_2\text{O}$, separates in white, monoclinic crystals, which rapidly effloresce, and are soluble in water but not in alcohol. The barium salt is formed in the usual way, and from it oxalostannic acid can be obtained. It crystallises in nacreous scales, less soluble in water than oxalotitanic acid.

Silica does not yield analogous compounds.

C. H. B.

Action of Inorganic acid Metallic Oxides on Organic acids.

By A. ROSENHEIM (*Zeit. anorg. Chem.*, 4, 352—373).—Monobasic acids, such as formic, acetic, propionic, and benzoic acids, do not dissolve tungstic and molybdic acids. Oxalic acid dissolves both tungstic and molybdic acids. Malonic, succinic, and phthalic acids do not dissolve tungstic acid, and dissolve only a small quantity of molybdic acid. Bibasic and polybasic hydroxy-acids, such as malic acid, tartaric acid, &c., dissolve tungstic acid, although less readily than oxalic acid; but they easily dissolve molybdic acid. Monobasic hydroxy-acids, such as glycollic and lactic acids, behave like oxalic acid, but dissolve much smaller quantities of the metallic oxides. Salicylic acid dissolves only a small quantity of tungstic acid, but a considerable quantity of molybdic acid. Meta- and para-hydroxybenzoic acids are almost without action on molybdic acid. These results are in accordance with those obtained by Magnanini (*Abstr.*, 1891, 251; 1892, 256, 1265).

Action of Tungstic acid on Oxalic acid and on Oxalates.—When an excess of tungstic acid is added to a boiling solution of oxalic acid and the mixture allowed to remain, a colloidal solution is obtained, which is yellow by transmitted light, and has a greenish-yellow fluorescence. It undergoes no change, even if kept for four months; on concentration, it deposits oxalic acid, and then entirely decomposes with precipitation of tungstic acid.

A double salt of the constitution $\text{COOK} \cdot \text{COO} \cdot \text{WO}_2 \cdot \text{OK} + \text{H}_2\text{O}$ is obtained by dissolving tungstic acid in a solution of normal potassium oxalate. It crystallises in white, microscopic tablets, is very sparingly soluble in water, has an acid reaction, and, when boiled with strong hydrochloric or sulphuric acid, gives a precipitate of tungstic acid. When boiled with vanadic acid, it gives a deep yellow coloration. It is also easily obtained by boiling hydrogen potassium oxalate with the theoretical quantity of a melt of potassium carbonate and tungstic anhydride. The corresponding *sodium* and *ammonium* salts have been prepared; they are similar to the potassium salt, but are very soluble.

When tungstic acid is dissolved in solutions of the acid oxalates, crystalline mixtures of potassium ditungstate and acid potassium oxalate of the composition $x(\text{K}_2\text{O}, 2\text{C}_2\text{O}_3) + y(\text{K}_2\text{O}, 2\text{WO}_3)$ are obtained, from which hydrogen potassium oxalate can be separated by crystallisation.

Action of Molybdic acid on Oxalic acid and on Oxalates.—The acid

$\begin{smallmatrix} \text{OO} \\ | \\ \text{COO} \end{smallmatrix} > \text{MoO}_2 + 3\text{H}_2\text{O}$ is obtained by boiling an excess of molybdic acid with a solution of oxalic acid, evaporating to a syrup, and then dissolving in a small quantity of water containing a few drops of nitric acid. The compound has already been described by Péchard (Abstr., 1889, 858).

Two compounds are obtained by saturating a boiling solution of ammonium oxalate with molybdic acid. The one crystallises in sparingly soluble crusts, decomposes on recrystallisation, and has the composition $\text{C}_2\text{O}_2(\text{O} \cdot \text{MoO}_2 \cdot \text{ONH}_4)_2$; the other forms easily soluble, white needles, can be recrystallised without decomposition, and gives a yellow coloration when boiled with vanadic acid. It has the constitution $\text{COONH}_4 \cdot \text{COO} \cdot \text{MoO}_2 \cdot \text{ONH}_4 + \text{H}_2\text{O}$.

When potassium oxalate is boiled with an excess of molybdic acid, potassium trimolybdate is formed, together with a small quantity of the salt $\text{K}_2\text{O}, \text{MoO}_3, \text{C}_2\text{O}_3 + \text{H}_2\text{O}$. The latter is easily obtained by boiling potassium molybdate with oxalic acid in molecular proportion.

The salt, $\text{K}_2\text{O}, 2\text{MoO}_3, \text{C}_2\text{O}_3$, is obtained by dissolving a melt of potassium carbonate (1 mol.) with molybdic anhydride (2 mols.) in a solution of oxalic acid (1 mol.). It crystallises in sparingly soluble white crusts.

Sodium oxalate reacts with molybdic acid in the same way as the potassium salt. The salt $\text{COONH}_4 \cdot \text{COO} \cdot \text{MoO}_2 \cdot \text{ONa} + 2\text{H}_2\text{O}$ is obtained by the action of hydrogen ammonium oxalate (1 mol.) on sodium dimolybdate (1 mol.). It crystallises in large, lustrous prisms.

The salt $\text{COONH}_4 \cdot \text{COO} \cdot \text{MoO}_2 \cdot \text{OH} + \text{H}_2\text{O}$ is obtained by boiling an excess of molybdic acid with hydrogen ammonium oxalate. It crystallises in prisms, and does not reduce vanadic acid. The corresponding potassium salt is obtained in a similar way. The sodium salt could not be obtained.

Action of Vanadic acid on Normal Oxalates.—When vanadic acid is boiled with solutions of normal alkali oxalates, deep yellow solutions are obtained, which, on concentration, deposit red acid vanadates and large yellow prisms of oxalovanadates. The two compounds are separated mechanically.

The ammonium salt, $3(\text{NH}_4)_2\text{O}, \text{V}_2\text{O}_5, 4\text{C}_2\text{O}_3 + 4\text{H}_2\text{O}$, the potassium salt, $3\text{K}_2\text{O}, \text{V}_2\text{O}_5, 4\text{C}_2\text{O}_3 + 6\text{H}_2\text{O}$, and the sodium salt, $3\text{Na}_2\text{O}, \text{V}_2\text{O}_5, 4\text{C}_2\text{O}_3 + 6\text{H}_2\text{O}$ have been prepared. The author assigns to them the constitution $\text{V}_2\text{O}_2(\text{OR})_2(\text{O} \cdot \text{CO} \cdot \text{COOR})_4 + x\text{H}_2\text{O}$. They are easily obtained pure by the action of 1 mol. of a normal vanadate, $\text{R}_2\text{OV}_2\text{O}_5$, on 4 mols. of an acid oxalate.

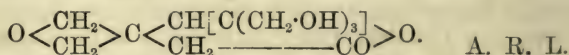
E. C. R.

Preparation of Amylic Pyruvate. By L. SIMON (*Bull. Soc. Chim.* [3], 9, 136—137).—Amylic pyruvate, $\text{CH}_3 \cdot \text{CO} \cdot \text{COO} \cdot \text{C}_5\text{H}_{11}$, is prepared by heating a mixture of amyl alcohol with anhydrous pyruvic acid in molecular proportion for several hours in a reflux apparatus under reduced pressure; the product is then slowly distilled from the water bath under a pressure of 10—15 mm., using a fractionating column. The yield is 99 per cent. of the theoretical.

J. B. T.

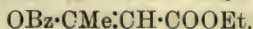
Synthesis of a Lactone from Formaldehyde and Pyruvic acid. By H. HOSAEUS (*Annalen*, 276, 79—82).—The lactone $\text{O} \begin{array}{c} | \\ \text{O} \text{---} \text{CH}_2 \\ | \\ \text{CO} \cdot \text{CH}(\text{OH}) \end{array} > \text{C}(\text{CH}_2\text{OH})_2$, is prepared by heating pyruvic acid (1 mol.) with formic acid (4 mols.) in presence of water and calcium hydroxide; it crystallises from alcohol in white prisms, melts at 184° , and is very easily soluble in water. When boiled with alkalis, it yields salts of the acid $\text{C}_6\text{H}_{12}\text{O}_6$. The calcium salt is a micro-crystalline substance. Unlike pyruvic acid, the lactone does not yield a compound with phenylhydrazine, and it furnishes no iodoform when treated with iodine and soda. A. R. L.

Synthesis of a Lactone from Formaldehyde and Levulinic acid. By P. RAVE and B. TOLLENS (*Annalen*, 276, 69—75).—The lactone $\text{C}_{10}\text{H}_{16}\text{O}_6$ is obtained by keeping a mixture of levulinic acid (50 grams), 40 per cent. formaldehyde (250 grams), water (5 litres), and barium hydroxide (200 grams) for 14 days with frequent shaking, subsequently heating it to boiling, removing the barium by means of sulphuric acid, and evaporating the filtrate, when it separates in rhombic tablets. It has a bitter taste, melts at $174\text{--}176^\circ$, and emits a penetrating odour when ignited on platinum foil. A molecular weight determination by the cryoscopic method showed that the above is the molecular formula. The triacetyl derivative, $\text{C}_{10}\text{H}_{13}\text{O}_3(\text{OAc})_3$, melts at 161° . The authors submit the following constitutional formula for the lactone,



Preparation of Mucic acid from Gum Arabic. By E. MAUMENÉ (*Bull. Soc. Chim.* [3], 9, 138—142).—The variable yield of mucic acid is partly attributable to the fact that little attention is generally paid to the concentration and proportion of the nitric acid employed, and partly to the actual condition of the gum. The author discusses the first of these points at length, and gives details of previous work on the subject; he considers that gum arabic is a mixture of two varieties, which he designates by α - and γ -; both of these undergo condensation on heating or by the action of sulphuric acid, and it is from this condensation compound that mucic acid is chiefly or wholly obtained. By previously heating the gum at 165° and treating it with a dilute nitric acid not in large excess, it yielded as much as 65—69 per cent. of mucic acid. Both “condensed” and “uncondensed” gum are present in wine residues, and it is possible that the above facts may throw light on the difficulty of obtaining a constant weight of wine residues at 100° . J. B. T.

Ethyl Acetoacetate. By J. U. NEF (*Annalen*, 276, 200—245; compare Abstr., 1892, 140).—By the action of benzoic chloride on the metallic derivatives of ethyl acetoacetate there are obtained ethyl acetoacetate, ethyl α -benzoyl- β -hydroxyisocrotonate, ethyl dibenzoylacetoacetate, and ethyl β -benzoxyisocrotonate,



The last-named compound crystallises in colourless needles, melts at 43° , decomposes when heated with alcoholic sodium ethoxide into ethylic benzoate and ethylic sodacetoacetate, and yields β -benzoyl-phenylhydrazine and, perhaps, phenylmethylpyrazolone when treated with an ethereal solution of phenylhydrazine; when bromine is added to its solution in chloroform, cooled to -15° , a dibromide appears to be first formed, but hydrogen bromide is subsequently liberated, and the final products are ethylic bromacetoacetate and benzoic bromide.

The neutral compound formed by the action of acetic chloride on the metallic derivatives of ethylic acetoacetate is not ethylic triacetylacetate as previously stated (*loc. cit.*), but *ethylic β -acetoxyisocrotonate*, $\text{OAc}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COOEt}$. The compound absorbs bromine (1 mol.) at -15° , but soon afterwards hydrogen bromide is evolved, and the ultimate products are ethylic α - and γ -bromacetoacetate and acetic bromide. Ethylic β -acetoxyisocrotonate is also formed on boiling ethylic acetoacetate with acetic anhydride.

The author confirms Claisen's observation (Abstr., 1892, 1070) that his so-called ethylic acetylcarbintricarboxylate (*loc. cit.*) is *ethylic β -carbethoxyisocrotonate* (ethylic carboxyethylacetoacetate). This compound absorbs bromine (1 mol.) at -10° , but the *dibromide* produced is partially decomposed on distillation even under diminished pressure.

Ethylic β -carbethoxyacrylate, $\text{COOEt}\cdot\text{CH}\cdot\text{CH}\cdot\text{O}\cdot\text{COOEt}$, is obtained by treating ethylic sodioformylacetate suspended in ether with ethylic chlorocarbonate in the cold; it is a colourless oil having a pleasant odour, boils at 135° under a pressure of 25 mm., dissolves without alteration in nitric acid of 1.5 sp. gr., and forms a fairly stable *dibromide*.

Ethylic acetoxyfumarate, $\text{COOEt}\cdot\overset{\text{H}}{\underset{\text{H}\cdot\text{C}\cdot\text{COOEt}}{\text{C}}}\cdot\text{OAc}$, is the portion of the product insoluble in alkali obtained when acetic chloride is added to ethylic sodoxalacetate suspended in ether; it boils at 150° under a pressure of 18 mm., and is decomposed by sodium ethoxide and ethylic acetate and ethylic sodoxalacetate; it absorbs bromine (1 mol.) at -15° , but the *dibromide* decomposes yielding ethylic α -bromo- β -hydroxyfumarate (Wislicenus' ethylic bromoxalacetate, Abstr., 1890, 133). The portion which is soluble in alkalis of the above-mentioned product of the action of acetic chloride on ethylic sodoxalacetate, is a mixture of ethylic oxalacetate and

ethylic α -acetyl- β -hydroxyfumarate, $\text{COOEt}\cdot\overset{\text{H}}{\underset{\text{Ac}\cdot\text{C}\cdot\text{COOEt}}{\text{C}}}\cdot\text{OH}$. The latter is

a colourless oil, boils at 134 – 136° under a pressure of 10 mm., and decomposes carbonates in the cold; an alcoholic solution gives a deep red coloration with ferric chloride. Compounds similar to those just described are obtained from ethylic sodoxalacetate and benzoic chloride. Ethylic oxalacetate is identical with ethylic hydroxyfumarate, for the author finds that the above-described ethylic acetoxyfumarate is obtained from it by direct acetylation. When ethylic oxalacetate is treated with phosphoric chloride at 50° , ethylic chloro-

fumarate is obtained, which, when hydrolysed with alcoholic potash, yields chlorofumaric acid (Perkin, *Trans.*, 1888, 697).

Ethylic ethoxyfumarate, $\text{COOEt} \cdot \overset{\text{H}}{\underset{\text{H}}{\text{C}}} \cdot \text{COOEt}$, obtained by gradually adding ethylic iodide to the silver derivative of ethylic oxalacetate, is an oil of pleasant odour; its sp. gr. is 1.06 at 22°, it boils at 130° under a pressure of 11 mm. or at 136° under 16 mm. pressure. It gives no coloration with ferric chloride, and differs, therefore, from ethylic α -ethyl- β -hydroxyfumarate (Arnold, *Annalen*, 246, 337; *Abstr.*, 1888, 1179). The compound absorbs bromine (1 mol.) at -15°, and on distilling the *dibromide*, it decomposes into ethylic α -bromo- β -ethoxyfumarate boiling at 160° under a pressure of 17 mm., and apparently ethyl bromovinyl ether, carbonic anhydride being evolved.

When an alcoholic solution of ethylic ethoxyfumarate is treated in the cold with sodium ethoxide (2 mols.), the sodium salt which separates is dissolved in water, and the solution acidified, *hydroxyfumaric acid*, $\text{COOH} \cdot \overset{\text{H}}{\underset{\text{H}}{\text{C}}} \cdot \text{COOH}$, is obtained; it melts at 172° with decomposition, and its aqueous solution gives a dark red coloration with ferric chloride; when treated with phenylhydrazine hydrochloride in aqueous solution, phenylpyrazolonecarboxylic acid (Wislicenus, *Abstr.*, 1888, 1178) is formed.

When the silver derivative of ethylic α -acetyl- β -hydroxyisocrotonate is suspended in ether and treated in the dark with ethylic iodide, the portion of the product soluble in alkalis consists chiefly of ethylic α -acetylacetoacetate. When the portion which is insoluble in alkalis is heated on the water-bath with alcoholic sodium ethoxide, it gives Friedrich's ethoxyisocrotonic acid (*Annalen*, 219, 328), but if treated in the cold with the same reagent, an oil is obtained boiling at 190–195°, and having the odour of ethylic α -ethylacetoacetate. A lengthy discussion of these results concludes the paper.

A. R. L.

Organic Electrosyntheses. By S. P. MULLIKEN (*Amer. Chem. J.*, 15, 523–533; compare Crum Brown and Walker, *Abstr.*, 1891, 1192).—The compounds chosen for this investigation are the ketonic derivatives, like acetylacetone and ethylic acetoacetate. The products obtained by the electrolysis of such compounds are formed by the combination of the anions, so that they are identical with products which are obtained by treating the silver or sodium derivatives of the same compounds with iodine. The electrolytic cell consisted of a glass cylinder surrounded by a water cooler, rendered necessary by the high resistance of the electrolyte. The anodes were spirals of platinum wire, 1–2 mm. in diameter, and the cathodes rectangular strips of platinum foil, almost wide enough, when folded into cylinders, to surround the anodes. The current used was $\frac{1}{15}$ — $\frac{1}{3}$ ampère.

The electrolysis of diethylic sodiomalonate yields tetrethylic ethanetetra-carboxylate. Ethylic sodiomethanetricarboxylate yields *hexethylic ethanehexacarboxylate*, $\text{C}(\text{COOEt})_3 \cdot \text{C}(\text{COOEt})_3$, which forms white crystals, melts at 101° (corr.) and is freely, but slowly, soluble in alcohol and in ether.

The electrolysis of acetylacetone might be expected, if Perkin's views as to its hydroxyketonic character (*Trans.*, 1892, 816) be correct, to yield a "tetracetylene." The compound actually obtained is provisionally termed *tetracetylene* by the author, and is regarded

as having the constitution
$$\begin{array}{c} \text{OH} \cdot \text{CMe} \cdot \text{C} \cdot \text{COMe} \\ | \\ \text{OH} \cdot \text{CMe} \cdot \text{C} \cdot \text{COMe} \end{array}$$
 It crystallises in colour-

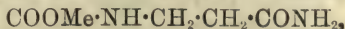
less cubes, melts at 191.2° (corr.), and is very sparingly soluble in cold alcohol. It is a feeble acid, and readily absorbs bromine. The same compound was prepared by treating the sodium derivative of acetylacetone with iodine, and its constitution was, to a certain extent, confirmed by the formation of condensation products; thus, when boiled with ammonium acetate solution, and then with dilute sulphuric acid and a pine-splinter, it yields Knorr's pyrroline reaction, showing that 5 : 2-dimethyl-3 : 4-diacetylpyrroline has been formed. So, also, on treatment with strong sulphuric acid, it yields the condensation product 2 : 5-dimethyl-2 : 3-diacetylfurfuran, which crystallises in white, felted needles, melts at 63° , and dissolves in boiling water.

The electrolysis of ethylic acetoacetate might be expected to yield ethylic diacetosuccinate, for this compound is the product of the action of iodine on the sodium derivative. It was found difficult to isolate the ethylic diacetosuccinate from the other products of the electrolysis, but it was undoubtedly present. A. G. B.

Nitrogen Halogen Compounds. By F. LENGFELD and J. STIEGLITZ (*Amer. Chem. J.*, 15, 504—518).—The authors prepared *methylic methocarbonyl-β-amidopropionate*, $\text{COOMe} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOMe}$, from methylic β-amidopropionate and methylic chloroformate, and found that it is identical with the main product of the action of sodium methoxide and methyl alcohol on bromosuccinimide (methylic methoxysuccinamic acid, this vol., i, 310), whose constitution is thus settled. When this compound is treated with hydrochloric acid, β-amidopropionic acid hydrochloride, $\text{HCl} \cdot \text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$, is produced; it forms white, irregular plates, and melts at 122.5° . β-Amidopropionic acid melts, with decomposition, at 206° (Hoogewerff and Van Dorp, *Abstr.*, 1891, 1216, give 196° ; Mulder gives 180°); an improvement in Hoogewerff and Van Dorp's method for preparing this acid (*loc. cit.*) is described. The *sulphate* of this acid crystallises in short, thick prisms, melts, with some decomposition, at 150° , and dissolves easily in water, but only sparingly in alcohol.

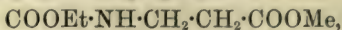
Methylic β-amidopropionate *hydrochloride* crystallises in lustrous, hygroscopic scales, and melts at $94\text{--}95^\circ$. The hydrochloride of the ethylic salt crystallises in white plates, melts at 65.5° , and dissolves easily in water, alcohol, and chloroform.

Methocarbonyl-β-amidopropionic acid has already been described as methoxysuccinamic acid (this vol., i, 310). The *barium* and *silver* salts are described; the *ethylic* salt is a colourless oil which solidifies in a freezing mixture, and melts at 15.5° . The *amide*,



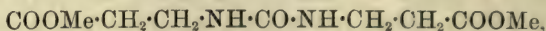
crystallises in colourless, broad, orthorhombic plates, with sharply defined lines of cleavage; it melts at 142.5° .

Methylic ethoxycarboxyl-β-amidopropionate,



prepared by treating methylic β-amidopropionate hydrochloride with silver oxide and ethylic chloroformate, is an oil which boils at 134—137° (15 mm.), and melts below 0°. The *acid* itself forms colourless crystals, melting at 59°. The *amide* also forms colourless crystals, and melts at 120·5°.

Dimethylic succino-β-ureidopropionate,



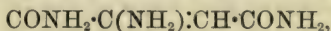
melts at 65·5°. By mild hydrolysis, it yields succinic acid and β-ureidopropionic acid. Concentrated hydrochloric acid decomposes it into succinic acid and β-lactylcarbamide.

Methylic β-ureidopropionate, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOMe}$, is obtained by the action of potassium cyanate on methylic amidopropionate hydrochloride; it forms colourless, long, flat prisms, melts at 66·5°, and is easily soluble in water, alcohol, and chloroform. *β-Ureidopropionic acid* melts with evolution of gas at 170—171°; it is very unstable, readily losing water with formation of β-lactylcarbamide; the *potassium salt* was prepared and found to be very hygroscopic, and to melt at 100°.

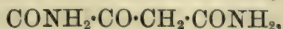
β-Lactylcarbamide, $\begin{array}{c} \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \\ | \quad | \\ \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \end{array}$, melts at 272° with decomposition; it is neutral and insoluble in sodium carbonate, but soluble in caustic alkalis. The *silver derivative*, $\begin{array}{c} \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \\ | \quad | \\ \text{CH}_2 \cdot \text{CO} \cdot \text{N}^+\text{Ag} \end{array}$, was prepared.

A. G. B.

Amidomaleamide and Oxysuccinamide. By R. T. MAMERT (*Compt. rend.*, 117, 167—170).—Amidomaleamide,



is formed by the action of aqueous ammonia on ethylic chlorofumarate in the cold; after two days, the amide crystallises out in dull, opaque, yellowish, prismatic crystals, melting, with decomposition, at 190—195°. It is decomposed by hot alkalis, and is hydrolysed by cold alkalis into the *alkali amidomaleamate*, $\text{CONH}_2 \cdot \text{C}(\text{NH}_2) \cdot \text{CH} \cdot \text{COOR}$. The corresponding *copper salt* is described. When treated with hot aqueous phenylhydrazine acetate, ammonia is eliminated, and *phenylhydrazo-succinamide*, $\text{NHPh} \cdot \text{N} \cdot \text{C}(\text{CONH}_2) \cdot \text{CH}_2 \cdot \text{CONH}_2$, is formed; this crystallises in colourless needles, is optically active, and melts, with decomposition, at 180°. When amidomaleamide is hydrolysed with dilute sulphuric acid, it is transformed into *oxysuccinamide*,



which crystallises in small, colourless needles, and melts, with decomposition, at 180°. It gives a characteristic red coloration with ferric chloride, and with copper sulphate and phenylhydrazine acetate, yields the amidomaleamate and hydrazone mentioned above. Sodium amalgam converts it into malic acid.

JN. W.

Essential Oil of Cochlearia armoracia. By G. SANI (*Real. Accad. Linc.*, 1892, ii, 17—18).—A glucoside contained in *Cochlearia armoracia* undergoes hydrolysis when the bruised roots, gathered during the autumn or winter, are left for 24 hours in contact with water; the essential oil and a little sulphur are then extracted with ether. On evaporating the ethereal solution, a residue of allylthiocarbimide is obtained; the roots therefore contain potassium myronate.

W. J. P.

Isomeric Thetines. By G. CARRARA (*Gazzetta*, 23, i, 493—509; compare Brown and Letts, *Trans. Edin. R. Soc.*, 28, 561).—*Methylethylthetine bromide*, $\text{SMeEtBr}\cdot\text{CH}_2\text{COOH}$, is readily prepared by the action of bromacetic acid on methylic ethylic sulphide in the cold; it forms highly deliquescent, rhombohedral-shaped crystals melting at 84° with decomposition, and is soluble in alcohol, but not in ether or benzene. It has an acid reaction, and is shown by cryoscopic determinations to undergo dissociation in aqueous solution. The corresponding *platinochloride*, $(\text{C}_5\text{H}_{10}\text{O}_2\text{S})_2\cdot\text{H}_2\text{PtCl}_6$, forms red, orthorhombic crystals, $a : b : c = 0.9462 : 1 : 1.0133$, which melt at 167° with decomposition. *Methylethylthetine*, $\text{SMeEt}\langle\overset{\text{O}}{\text{CH}_2}\rangle\text{CO}$, is ob-

tained by treating the aqueous solution of its bromide with moist silver oxide, and distilling off the water under reduced pressure. It is a white, deliquescent substance, and is neutral to litmus; cryoscopic experiments in water and acetic acid, and boiling point determinations of alcoholic solutions, seem to indicate that the anhydride does not become hydrated in aqueous solution.

Dimethyl- α -propionylthetine bromide, $\text{SBrMe}_2\cdot\text{CHMe}\cdot\text{COOH}$, an isomeride of the preceding bromide, is obtained from methylic sulphide and α -bromopropionic acid. It forms small, rectangular tablets melting at 84 — 85° with decomposition, and is very deliquescent; cryoscopic determinations show it to be completely dissociated in aqueous solutions. The *platinochloride*, $(\text{C}_5\text{H}_{10}\text{O}_2\text{S})_2\cdot\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$, forms monosymmetric prisms, $a : b : c = 2.313 : 1 : 3.051$; $\beta = 83^\circ 23'$, which melt at 105 — 106° . Its purification is difficult, owing to intermixture with the platinochlorides of dimethylethylsulphine and trimethylsulphine; these sulphines are produced by decomposition of the thetine during the evaporation of its aqueous solution. *Dimethyl-*

α -propionylthetine, $\text{SMe}_2\langle\overset{\text{O}}{\text{CHMe}}\rangle\text{CO}$, is obtained by treating the aqueous solution of the bromide with moist silver oxide; it is a very deliquescent, white substance, and gives similar results to its isomeride in cryoscopic determinations.

Dimethyl- β -propionylthetine bromide, $\text{C}_5\text{H}_{11}\text{O}_2\text{SBr}$, is prepared by heating a mixture of β -bromopropionic acid and methylic sulphide. It is less deliquescent than its isomerides, and forms beautiful, white needles which melt at 115° with decomposition. The *platinochloride*, $(\text{C}_5\text{H}_{10}\text{O}_2\text{S})_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in anhydrous anorthic needles, $a : b : c = 1.087 : 1 : 1.071$; $\alpha = 77^\circ 35'$, $\beta = 121^\circ 42'$, $\gamma = 101^\circ 31'$. The thetine itself could not be prepared in a pure state, being much less stable than its isomerides.

W. J. P.

Synthesis of Mercaptothiazoles. By A. MIOLATI (*Gazzetta*, 23, i, 575—580).—The author has succeeded in synthesising the mercaptothiazoles by an extension of the process by which he determined the constitution of the so-called rhodanic acid (*Abstr.*, 1891, 943); the new method depends on a condensation of the α -halogenated ketones with ammonium dithiocarbamate.

Ethyllic methylmercaptothiazolecarboxylate, $N \begin{smallmatrix} \text{C}(\text{SH}) \cdot \text{S} \cdot \text{COOEt} \\ \text{CMe} = \text{C} \end{smallmatrix}$, is

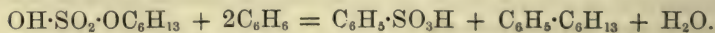
obtained on heating ammonium dithiocarbamate with ethylic chloroacetate; it forms white needles melting at 141° , and is insoluble in water, but soluble in alcohol or ether. Its alcoholic solution precipitates salts of silver and mercury. On dissolving it in potash and acidifying the solution, the corresponding *acid* separates; it is obtained as a crystalline powder which melts at 211 – 212° with decomposition, and is soluble in alcohol, ether, or boiling water.

On heating ammonium dithiocarbamate with chloracetone in alcoholic solution, *methylmercaptothiazole*, $N \begin{smallmatrix} \text{C}(\text{SH}) \cdot \text{S} \\ \text{CMe} = \text{CH} \end{smallmatrix}$, is obtained; it melts at 89 – 90° , and is soluble in the ordinary organic solvents.

Phenylmercaptothiazole, $N \begin{smallmatrix} \text{C}(\text{SH}) \cdot \text{S} \\ \text{CPh} = \text{CH} \end{smallmatrix}$, is prepared by the action of ammonium dithiocarbamate on bromoacetophenone; it forms monosymmetric crystals which melt at 168° . It is accompanied by a substance melting at 114° , possibly dithiocarbamineacetophenone.

W. J. P.

Condensation of Aliphatic Alcohols with Aromatic Hydrocarbons. By A. BROCHET and P. LE BOULENGER (*Compt. rend.*, 117, 235—238).—When benzene (1 part) is heated with alcohol (2 parts) and sulphuric acid (4 parts) in a sealed tube at 175 – 200° for 3–4 hours, ethylbenzene, boiling at 137° , and hexethylbenzene, melting at 123° , are formed. Similar results are obtained with normal propyl alcohol, hexapropylbenzene, melting at 118° , being formed, as well as liquid hydrocarbons, boiling at 210 – 240° . The yield of mixed hydrocarbons is 50 per cent. Isobutyl alcohol yields a butylbenzene, boiling at 167 – 168° , and a dibutylbenzene, boiling at 230 – 240° . The mechanism of the reaction appears to be exhibited in the case of hexyl alcohol, benzenesulphonic acid being formed, and recognised by conversion into its calcium salt and into phenol. The hydrogen hexylic sulphate first formed appears to react with the benzene according to the equation



Hydrogen alkyl sulphates, however, when separately prepared, do not seem to have any such action on benzene; neither do the aromatic sulphonic acids react with the alcohols.

JN. W.

Ethereal Oil of the Seeds of *Cicuta virosa*. By J. TRAPP (*Arch. Pharm.*, 231, 212—213).—In 1858 the author prepared an ethereal oil by distillation of the dried seeds of *Cicuta virosa* with

water; it resembles Roman cumin oil in taste and odour, and consists chiefly of cymene and cuminaldehyde.

J. B. T.

Condensation of Hydrocarbons of the Benzene Series with those of the Ethylene Series. By A. BROCHET (*Compt. rend.*, 117, 115—118).—Crystallisable benzene is mixed with a small quantity of normal α -hexylene and agitated with about 10 per cent. of ordinary sulphuric acid; development of heat and evolution of sulphurous anhydride ensue, and the liquid blackens. When the action ceases, a further quantity of hexylene is added, and this process is continued until 1 part of hexylene has been added for every 2 parts of benzene. The acid must be renewed at least once towards the end of the operation. The upper layer of liquid is decanted and washed first with water and afterwards with sodium hydroxide solution, and fractionated; the product is hexylbenzene, formed simply by direct combination, and the yield is about 50 per cent. It is a colourless, mobile liquid, boiling at 208° under ordinary pressure; sp. gr. at $15^\circ/4^\circ = 0.869$; refractive index $n = 1.492$; molecular refractive power (new formula) = 53.93. It combines with bromine in the cold, with immediate evolution of hydrogen bromide. It yields a monosulphonic acid, the barium salt of which crystallises with $2\text{H}_2\text{O}$ in large, nacreous lamellæ, soluble in water or alcohol, especially on heating. The calcium salt is similar.

Hexylbenzene reduces potassium manganate and permanganate slowly in the cold, and more rapidly on heating; the molecule seems to be completely broken up, and only a small quantity of oxalic acid is obtained. Nitric acid, somewhat diluted, yields benzoic acid, and if the hydrocarbon is allowed to fall drop by drop into a boiling solution of chromic acid mixture, formic acid is one of the products of oxidation. It would seem, therefore, that this hexylbenzene is methylbutyltoluene or methylbutylphenylmethane.

This method of synthesis is a general one. Toluene behaves like benzene, but amylene gives less satisfactory yields than hexylene.

C. H. B.

Identity of the Hydrocarbon C_7H_{14} derived from Perseitol and from Resin Oil with Heptanaphthene. By L. MAQUENNE (*Bull. Soc. Chim.* [3], 9, 129—131).—The hydrocarbon C_7H_{14} is shown to be identical with heptanaphthene from Russian petroleum by a comparison of their colour reactions and physical constants; the former compound has, however, been shown to be hexahydrotoluene (compare Abstr., 1892, 1065), and it is also identical with that from essence of resin and with Markovnikoff's hydrocarbon from suberonyl alcohol (this vol., i, 13). Heptene is therefore a methyleyclohexane.

J. B. T.

A Decanaphthene from Caucasian Petroleum. By W. RUDEVITSCH (*J. pr. Chem.* [2], 48, 188—191).—The production of terpenes from naphthenes has not heretofore been effected; the author has again attempted it. A decanaphthene (b. p. $168\text{--}170^\circ$; sp. gr. at $0^\circ/0^\circ = 0.8073$) was chlorinated, whereby two chlorides, boiling respectively at $213\text{--}215^\circ$ and $215\text{--}218^\circ$, and of sp. gr. at $0^\circ/0^\circ$ of 0.9574 and 0.9644, were obtained. Both these chlorides were con-

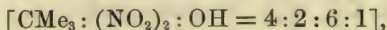
verted into naphthylenes, which boiled at 167—168° and 169—172° respectively; the former resembles Berkenheim's menthene (Abstr., 1892, 866). Besides these naphthylenes, *decanaphthenyl acetate*, $\text{CH}_3\text{COOC}_{10}\text{H}_{19}$, was prepared; it is colourless, viscid, and of fruity odour; it boils at 237·5—239·5° (corr.), and its sp. gr. at 0°/0° is 0·9323. On hydrolysis, it yields *decanaphthene alcohol*, which is colourless, viscid, and of characteristic odour; its sp. gr. at 0°/0° is 0·9064, and it boils at 223·5—225·5° (corr.); the action of carbanil on this alcohol gives rise to vitreous needles which melt at 232—234°.

To obtain a $\text{C}_{10}\text{H}_{16}$ hydrocarbon, the two naphthylenes were mixed, converted into dibromides, and distilled with quinoline, but the original hydrocarbons were regenerated. When menthene dibromide is similarly treated, it yields a $\text{C}_{10}\text{H}_{16}$ hydrocarbon identical with that obtained from the same bromide by treatment with alcoholic potash (Berkenheim, *loc. cit.*). When the naphthylene boiling at 167—169° was heated with cupric sulphate according to Brühl's method (Abstr., 1892, 200), a hydrocarbon, $\text{C}_{20}\text{H}_{16}$ (b. p. 173—176°), was isolated.

The above reactions go to prove that the decanaphthene from petroleum is not identical with Berkenheim's menthonaphthene (Abstr., 1892, 866).
A. G. B.

Structure of Nitro-compounds and of the Oxides of Nitrogen. By A. L. POTILITZIN (*J. Russ. Chem. Soc.*, 25, 75—79).—The author considers it probable that aromatic nitro-compounds are derivatives of nitric acid, and contain the group $-\text{N} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix}$; whilst fatty nitro-compounds are derived from nitrous acid, containing the group $-\text{N} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix}$. Nitroles and nitrolic acids he considers to be derivatives of hyponitrous acid, with the group $-\text{N}:\text{O}$.
J. W.

Derivatives of Paratertiarybutylphenol. By K. JEDLICKA (*J. pr. Chem.* [2], 48, 97—112).—Dinitroparatertiarybutylphenol (m. p. 93°; Abstr., 1881, 898) has the constitution



for when treated with concentrated nitric acid it yields picric acid. The *methyl* derivative of this phenol, $\text{CMe}_3 \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{OMe}$, crystallises in pale-yellow laminae, melts at 101—102°, and dissolves easily in hot alcohol but not in water; when heated with aqueous ammonia at 120—130°, it affords a good yield of the corresponding dinitrobutylaniline (Abstr., 1888, 823). The *ethyl* derivative is similar in properties, but melts at 95—96°.

Triamidotertiarybutylbenzene $[\text{CMe}_3 : (\text{NH}_2)_3 = 4 : 2 : 6 : 1]$, resulting from the reduction of the dinitrobutylaniline, crystallises in flat, colourless prisms, which become brown on exposure to the air; it melts at 156—157° and dissolves in alcohol and in ether, but only sparingly in water; it is a bi-acid base. The *hydrochloride*, $\text{C}_{10}\text{H}_{17}\text{N}_3 \cdot 2\text{HCl}$, and *oxalate*, $\text{C}_{10}\text{H}_{17}\text{N}_3 \cdot \text{C}_2\text{H}_2\text{O}_4$, are described.

Triacetamidotertiarybutylbenzene $[\text{CMe}_3 : (\text{NHAc})_3 = 4 : 2 : 6 : 1]$

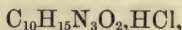
crystallises in colourless needles, melts at 220° , and dissolves freely in alcohol, but only sparingly in water and benzene.

As the amido-groups in this triamidobutylbenzene are adjacent, the compound condenses easily with orthodiketones to form phenazines.

Phenanthramidotertiarybutylphenazine, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \end{array} > \text{C}_6\text{H}_2(\text{CMe}_3) \cdot \text{NH}_2$,

forms orange-red needles, melts at 219 – 220° , and dissolves in hot alcohol, ether, and benzene, but not in water. *Benzilamidotertiarybutylphenazine*, $\text{C}_2\text{N}_2\text{Ph}_2 \cdot \text{C}_6\text{H}_4(\text{CMe}_3) \cdot \text{NH}_2$, crystallises in yellow needles, melts at 124 – 125° , and resembles the preceding phenazine in its behaviour towards solvents.

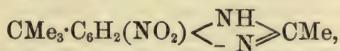
Nitrodiamidotertiarybutylbenzene crystallises in red needles, melts at 104 – 105° , and dissolves sparingly in water, but freely in alcohol or ether. It is a feeble, mon-acid base; the *hydrochloride*,



and *sulphate*, $(\text{C}_{10}\text{H}_{15}\text{N}_3\text{O}_2)_2 \cdot \text{H}_2\text{SO}_4$, are described. With orthodiketones, it yields phenazines such as *phenanthronitrotertiarybutylphenazine*, $\text{C}_{12}\text{H}_8 \cdot \text{C}_2\text{N}_2 \cdot \text{C}_6\text{H}_2(\text{CMe}_3) \cdot \text{NO}_2$, which crystallises in yellowish needles, melts at 235 – 236° , and dissolves freely in benzene; and *benzilitrotertiarybutylphenazine*, $\text{C}_2\text{N}_2\text{Ph}_2 \cdot \text{C}_6\text{H}_2(\text{CMe}_3) \cdot \text{NO}_2$, which forms brownish, lustrous laminae, melts at 195 – 196° , and behaves similarly towards solvents.

By azotising the diamido-compound, *nitrazimidotertiarybutylbenzene*, $\text{CMe}_3 \cdot \text{C}_6\text{H}_2(\text{NO}_2) < \begin{array}{c} \text{NH} \\ - \text{N} \end{array} > \text{N}$, is obtained; this crystallises in flesh-coloured laminae, melts at 205° (later, the m. p. 210 – 211° is given), and dissolves freely in alcohol and benzene, but not in water; it is feebly acid, yielding a crystalline *sodium* derivative, $\text{C}_{10}\text{H}_{11}\text{NaN}_4\text{O}$.

By treatment with acetic chloride, the nitrodiamidobutylbenzene yields *nitrotertiarybutylphenylenethenylamidine*,



which forms brownish prisms, melts at 258° , and dissolves sparingly in water, but freely in alcohol and in ether. The *hydrochloride*, $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_2 \cdot \text{HCl}$, was analysed. When concentrated formic acid is substituted for acetic chloride, *nitrotertiarybutylphenylenemethenylamidine*, $\text{CMe}_3 \cdot \text{C}_6\text{H}_2(\text{NO}_2) < \begin{array}{c} \text{NH} \\ - \text{N} \end{array} > \text{CH}$, is obtained; this crystallises in pale-brown tables and prisms, melts at 261° , and has the same solubility as the ethenyl base. With benzoic chloride, *dibenzoyldiamidonitrotertiarybutylbenzene*, $\text{CMe}_3 \cdot \text{C}_6\text{H}_2(\text{NHBz})_2 \cdot \text{NO}_2$, is obtained; this crystallises in white needles, melts at 245 – 246° , and dissolves in hot alcohol but not in water.

A. G. B.

Action of Sulphuric Acid on Catechol and on Homocatechol. By H. COUSIN (*Compt. rend.*, 117, 113–115).—When catechol is allowed to remain for several days in contact with twice its weight of concentrated sulphuric acid, it yields a monosulphonic acid, $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{SO}_3\text{H}$, the barium salt of which crystallises with $4\text{H}_2\text{O}$ in

small, rectangular prisms, soluble in water, but only slightly soluble in alcohol, whilst the potassium salt crystallises in anhydrous, silky needles, very soluble in water, but insoluble in cold alcohol. With ferric chloride, the solutions give a green coloration. The free acid crystallises in stellate groups of slender needles, which melt at $53-54^{\circ}$, are very deliquescent, dissolve in water and alcohol, and darken rapidly when exposed to light. This acid seems to be isomeric with that obtained by Barth and Schmidt by the action of fused potassium hydroxide on one of the disulphonated phenols.

When heated with sulphuric acid at 130° , catechol is partly decomposed, but, if heated for half an hour on a water bath with 5 parts of sulphuric acid containing 30 per cent. of the anhydride, it yields a disulphonic acid, $C_6H_2(OH)_2(SO_3H)_2$, which, when strongly cooled, crystallises in stellate groups of needles. The potassium salt crystallises with $1H_2O$ in small, oblique prisms, very soluble in water, but only slightly so in alcohol. The barium salt forms microscopic prisms, very slightly soluble in cold water, but somewhat more so in hot water.

Homocatechol yields only a monosulphonic acid even when the temperature and the proportion of sulphuric acid are varied, or if an acid containing 30 per cent. of anhydride is used. It crystallises in long needles melting at $93-94^{\circ}$, is deliquescent, very soluble in alcohol or ether, and becomes brown when exposed to light. The best results are obtained by heating the homocatechol on the water bath for four hours with twice its weight of sulphuric acid containing 30 per cent. of the anhydride. The barium salt crystallises with $3H_2O$ in small, brilliant, transparent, elongated prisms, very slightly soluble in cold water, more so in boiling water, insoluble in alcohol. The potassium salt crystallises with $1H_2O$ in spherical masses of slender needles, very soluble in water, and insoluble in boiling absolute alcohol. Both salts become rose-coloured when exposed to light.

C. H. B.

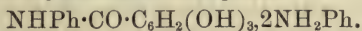
Derivatives of Phenylenediamine. By P. GUCCI (*Gazzetta*, **23**, i, 295—300; compare Abstr., 1888, 588).—Billetter and Steiner (Abstr., 1887, 366) have prepared orthophenylenethiocarbimide by the action of thionyl chloride on orthophenylenediamine; the author obtained it by heating the latter substance with carbon bisulphide and absolute alcohol in a sealed tube at 100° . It separates from alcoholic solution in iridescent plates melting at $296-297^{\circ}$ with slight decomposition. The para-isomeride, first prepared by Lellmann (*Annalen*, **221**, 9) may be obtained by an analogous method.

W. J. P.

Metallic Derivatives of Gallanilide. By P. CAZENEUVE (*Compt. rend.*, **117**, 47—50).—When a mixture of gallanilide and sodium hydroxide is dissolved in a very small quantity of hot water, gallanilide separates on cooling, and disodium gallanilide remains in solution, but cannot be crystallised. The liquid gradually blackens in consequence of oxidation. With calcium hydroxide or barium hydroxide solution, gallanilide yields a white precipitate containing only 1 atom of the metal, $NHPh \cdot CO \cdot C_6H_2(OH) : O_2M$. Zinc acetate

in aqueous solution yields the analogous zinc salt as an insoluble, white precipitate; but if this is dissolved in excess of gallanilide, it yields the monobasic salt, which crystallises in yellowish plates. If, on the other hand, zinc acetate in the proper proportion is added to a solution of gallanilide, containing just sufficient ammonia to neutralise the whole of the acetic acid, the tribasic zinc salt is obtained. Lead acetate yields only the bibasic salt; mercuric and cupric acetates give no definite products.

Gallanilide yields insoluble precipitates with alkaloids, and with aniline it forms the crystallisable compound



C. H. B.

Decomposition of Diazobenzene Sulphate in Isoamyl Alcohol. By W. R. ORNDORFF and C. G. HOPKINS (*Amer. Chem. J.*, **15**, 518—523).—The mixture of diazobenzene sulphate and isoamyl alcohol was heated below 100°, using a reflux condenser. The products of the reaction were found to be phenol, isoamyl phenyl ether, benzene, isovaleraldehyde, nitrogen, and sulphuric acid. When metanitrodiazobenzene sulphate was similarly treated, nitrobenzene, isovaleraldehyde, nitrogen, and much metadinitrohydroxyazobenzene, but no metanitrophenol, were found among the products of the decomposition.

A. G. B.

Reaction of Alcohols with Paradiazobenzenesulphonic acid. By W. B. SHOBER (*Amer. Chem. J.*, **15**, 379—391; compare this vol., i, 325).—The alcohols were heated with the acid at different pressures, and the products identified by conversion into amides through the chlorides. The following conclusions as to the course of the reactions are drawn:—(1.) When paradiazobenzenesulphonic acid is decomposed with methyl alcohol under diminished pressure, benzenesulphonic acid alone is produced. (2.) At the ordinary pressure both benzenesulphonic acid and paramethoxybenzenesulphonic acid are formed. (3.) At a *plus* pressure of 350 mm. both products are formed. (4.) At a *plus* pressure of 850 mm. both compounds are formed, but the methoxy-acid predominates. (5.) At a pressure of about 30 atmospheres the methoxy-acid alone is produced. (6.) When ethyl alcohol is used at various pressures up to 850 mm., benzenesulphonic acid alone is produced. (7.) When propyl alcohol is used under the same conditions, benzenesulphonic acid only is formed.

Paramethoxybenzenesulphonamide crystallises in long, slender needles, melts at 113°, and is soluble in hot water and in alcohol; when attacked by fuming nitric acid, it is converted into metadinitrobenzene.

For the preparation of anisoil the author recommends that diazobenzene nitrate and methyl alcohol be heated together until the temperature rises to 45°. Anisoil is converted into anisoildisulphonic acid by the action of ordinary concentrated sulphuric acid.

A. G. B.

Action of Phenylhydrazine on Ethylene Chlorhydrin. By U. ALVISI (*Gazzetta*, **23**, i, 529—535; compare *Abstr.*, 1892, 884).—On boiling a benzene solution of ethylene chlorhydrin with phenyl-

hydrazine, the hydrochloride of the latter is deposited and nitrogen is evolved; salts of ammonium, aniline, and glyoxaldiphenylhydrazine remain in solution.

W. J. P.

Constitution of Colouring Matters of the Rosaniline Group.

By PRUD'HOMME and C. RABAUT (*Compt. rend.*, 117, 40—42).—When a current of dry ammonia gas is passed over finely-powdered rosaniline hydrochloride, previously dried at 100° in a vacuum, there is development of heat, and the green, lustrous salt is converted into a violet-purple powder which finally becomes pale carmine. The first change corresponds with the absorption of 1 mol., and the final change with the absorption of 2 mols., of ammonia by 1 mol. of the salt. The whole of the absorbed gas is given off on gently heating, and even in the cold in a dry vacuum. Hexamethylrosaniline-violet, when treated in the same way, yields first an indigo-blue, and then a violet-grey product, strictly analogous in composition to the two compounds just described, and the whole of the ammonia is likewise given off in a dry vacuum in the cold. Aniline hydrochloride, under similar conditions, is completely decomposed by the ammonia which it absorbs, and, since the hydrochlorides of the secondary amines are less stable than those of the primary amines, the author regards these results as affording further support to Rosenstiehl's view that the rosanilines are not salts of amines.

C. H. B.

Nitroquinol. By K. ELBS (*J. pr. Chem.* [2], 48, 179—185).—*Nitroquinol* [$\text{NO}_2 : (\text{OH})_2 = 2 : 1 : 4$] is prepared by mixing orthonitrophenol (35 grams), sodium hydroxide (50 grams), and ammonium persulphate (50 grams; this vol., ii, 516) in water (1500 grams), intermittently shaking for $1\frac{1}{2}$ —2 days, acidifying with sulphuric acid, distilling off the unchanged nitrophenol with steam, and extracting the residue with ether. It crystallises in yellow or red rhombohedral granules or pyramids and melts at 133—134°; it sublimes with difficulty and dissolves best in alcohol and in ether. It forms two series of salts, which are soluble, with the exception of those of lead, copper, and silver; the solutions of the acid salts are brown, those of the normal salts, violet-blue. The *diacetyl* derivative [$\text{NO}_2 : (\text{OAc})_2 = 2 : 1 : 4$] crystallises in colourless laminæ or needles, melts at about 86°, and dissolves in hot alcohol, but not in water. The *dibenzoyl* derivative forms colourless needles, melts, but not sharply, at 140—142°, and dissolves best in hot benzene. Other derivatives, already known, were obtained.

The author recommends ammonium persulphate as an oxidising agent which can be applied in acid, alkaline, or neutral solutions, and has the advantage of not yielding a precipitate as a product of its reduction.

A. G. B.

Electrolysis of Substituted Organic Acids. By N. A. BUNGE (*J. Russ. Chem. Soc.*, 24, 690—694).—A solution of monochloroacetic acid (sp. gr. 1.250 at 15°) was electrolysed in a cell divided into two compartments by means of a membrane of parchment paper. The positive electrode was a platinum plate dipping into the solution in

one compartment, the negative electrode being mercury which was covered with mercuric oxide and a solution of sodium hydrogen carbonate in the other compartment. The mercuric oxide was introduced in order to prevent the possibility of the reduction of chloracetic acid to acetic acid and hydrogen chloride. The gas from the positive pole contained nothing but carbonic anhydride and chlorine. When an alkali salt was substituted for the free acid, no chlorine was evolved. Trichloroacetic acid gave similar results.

Sodium orthochlorobenzoate yielded oxygen only (and traces of carbonic anhydride), the free acid being deposited on the positive pole. No indication was obtained of chlorine or a chloride in the electrolysed solution. Potassium metanitrobenzoate behaved similarly, but with two platinum electrodes in an undivided cell, a portion of the hydrogen from the negative pole went to reduce the acid.

J. W.

Preparation of Orthochloro- and Orthobromo-benzoic acids.

By C. GRAEBE (*Annalen*, **276**, 54—57).—Orthochlorobenzoic acid is most advantageously prepared from anthranilic acid by Sandmeyer's method, observing the precautions described by Erdmann (this vol., i, 150). The yield is 90 per cent. of the theoretical. For the preparation of large quantities of orthochlorobenzoic acid, orthotoluidine is converted into orthochlorotoluene according to Erdmann's directions, and the latter oxidised by boiling it with dilute potassium permanganate solution; this method is obviously less convenient than the first, but the materials are cheaper.

Orthobromobenzoic acid is prepared from anthranilic acid in the same manner as the chlorinated acid; its preparation by oxidising orthobromotoluene is not satisfactory.

A. R. L.

Distinction between Isomeric Amidobenzoic acids and other Isomeric Compounds of the Benzene Series. By O. DE CONINCK (*Compt. rend.*, **117**, 118—120).—The isomeric amidobenzoic acids, nitrobenzoic acids, hydroxybenzoic acids, and the dihydric phenols can be distinguished by the behaviour of their alcoholic or ethereal solutions when exposed to light.

Amidobenzoic acids.—When the dry, solid acids are exposed to light, they undergo no change. In alcoholic solution the ortho-acid shows immediately a blue fluorescence, which persists throughout the insolation, whilst the liquid becomes reddish-brown; the meta-acid shows only a feeble blue fluorescence, and the liquid is bright red; the para-acid becomes pale yellow and eventually orange-yellow, without any fluorescence. In ethereal solution, the following changes are observed: *ortho*-, orange-red, soon changing to pale yellow; *meta*-, pale yellow, any undissolved acid which is in contact with the ether becoming brownish-red; *para*-, a somewhat thick, yellowish film is deposited, whilst the liquid is almost colourless. In diffused light, *ortho*-, reddish-brown, with formation of a deposit of the same colour on the walls of the tube; *meta*-, pale yellow in solution, whilst the solid acid becomes brownish-red where it is in contact with ether; *para*-, no change.

The solutions of orthamidobenzoic acid in various solvents also

show characteristic behaviour; in acetone, the liquid becomes claret coloured, in methyl alcohol, garnet-red, in chloroform, Solferino-red, in dilute hydrobromic acid, violet or amethyst.

Nitrobenzoic acids in the dry state do not change, but alcoholic solutions behave as follows: *ortho*-, colourless; *meta*-, yellow; *para*-, yellow. In ethereal solution, the changes are: *ortho*-, deep yellow and finally pale red; *meta*-, orange, with slight brown, translucent deposit; *para*-, yellow, with a thick, very adherent, orange-red deposit.

Hydroxybenzoic acids in ether undergo no change even after prolonged exposure, except that the *meta*-compound becomes very slightly yellow. Benzoic acid itself undergoes no change.

Dihydric phenols in ethereal solution behave as follows: resorcinol rapidly becomes yellow, then orange, and afterwards pale yellow, with a slight brownish-yellow deposit; catechol soon becomes deep yellow, then brown, and finally amber, without any deposit; quinol, after a long exposure, becomes only pale yellow and remains limpid.

C. H. B.

Mercuric Salicylates. By H. LAJOUX and A. GRANDVAL (*Compt. rend.*, 117, 44—47).—Normal mercuric salicylate, $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{COO})_2\text{Hg}$, is obtained as a white precipitate on the addition of a solution of mercuric chloride to a cold solution of sodium salicylate. It is decomposed by heat and is insoluble in water, but dissolves readily in solutions of sodium chloride, potassium cyanide, and potassium iodide, and has the general properties of mercuric salts. When boiled with water, it is converted into salicylic acid and the basic salicylate, $\text{C}_6\text{H}_4\langle\text{COO}\rangle\text{Hg}$, which can also be obtained by adding gradually to a boiling aqueous solution of the acid an equivalent quantity of freshly precipitated mercuric oxide, each successive portion being added when the yellow colour of the preceding portion has disappeared. Basic mercuric salicylate is a white powder, insoluble in water, alcohol, ether, or chloroform. When heated, it splits up into water, carbonic anhydride, phenol, mercury, &c. At a red heat a carbonaceous residue is left. The basic salicylate does not show the usual properties of mercuric salts. When suspended in cold water, it is not attacked by hydrogen sulphide until after many hours, but decomposition is more rapid if the liquid is heated. Alkali sulphides dissolve the basic salicylate completely, but the liquid gradually deposits a lemon-yellow precipitate, which very slowly turns black. The salt is slightly soluble in ammonia, very soluble in solutions of sodium hydroxide, sodium chloride, or potassium iodide, especially on heating, and the excess of salt separates in an amorphous form on cooling. All these solutions contain the unaltered salt. Even sodium hydroxide in hot concentrated solution does not decompose it, and hydrogen sulphide yields with the solution the yellow precipitate of mercuric sulphide and salicylate already mentioned. The solutions when dialysed yield the amorphous salt; they are all precipitated by acids and gradually become turbid when exposed to the air.

Cold concentrated hydrochloric acid acts very slowly on the basic salicylate, but the hot acid decomposes it at once. The dilute acid

dissolves it without change. Potassium cyanide also dissolves it, with formation of mercuric cyanide.
C. H. B.

Isoeugenolglycollic acid and Eugenolglycollic acid. By M. DENOZZA (*Gazzetta*, **32**, i, 553—559).—*Isoeugenolglycollic acid*, $\text{CHMe}:\text{CH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}$, is prepared by heating a mixture of eugenolglycollic acid (5 grams) with a solution of potash (5 grams) in absolute alcohol (15 grams) in a reflux apparatus for 24 hours at 100° , evaporating, and precipitating with hydrochloric acid. The conversion into the iso-acid is only partial, and there is some difficulty in separating the two. The purified iso-acid forms stellate groups of crystals, and melts at 116° . Isoeugenolglycollic acid is also obtained by acting on isoeugenol with monochloroacetic acid and caustic soda.

Barium isoeugenolglycollate, $(\text{C}_{12}\text{H}_{13}\text{O}_4)_2\text{Ba}\cdot 2\text{H}_2\text{O}$, loses its water at 115° . The corresponding *methylic* salt is a white, crystalline substance which melts at 90° and yields the *amide* by treatment with ammonia; the latter melts at 213° . No crystalline methylic salt could be obtained from eugenolglycollic acid.

Nitroisoeugenolglycollic acid, $\text{C}_{12}\text{H}_{13}\text{O}_4\cdot\text{NO}_2$, is prepared by direct nitration, and forms a yellow powder which, after a time, resinifies.

In the preparation of isoeugenol by Tiemann's method (*Abstr.*, 1892, 45), if the product formed by treating amyl alcohol and eugenol with caustic alkali is acidified before distillation in a current of steam, diisoeugenol is obtained, the yield being somewhat better than if Tiemann's process is followed.

Eugenolcinnamic acid, $\text{C}_3\text{H}_5\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{O}\cdot\text{C}(\text{COOH})\cdot\text{CHPh}$, may be prepared by heating a mixture of sodium eugenolglycollate, benzaldehyde, and acetic anhydride at 160° in a reflux apparatus; it forms large, anorthic prisms melting at 142° , is insoluble in water or acetic acid, and sparingly soluble in benzene. The *sodium* salt of this acid is anhydrous and only very sparingly soluble in water. The *barium* salt, $(\text{C}_{19}\text{H}_{17}\text{O}_4)_2\text{Ba}\cdot\frac{1}{2}\text{H}_2\text{O}$, and the *silver* salt were also prepared.

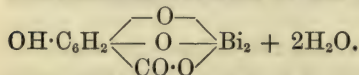
W. J. P.

Triacetyldibromogallic acid and Tribenzoyldibromogallic acid. By A. BIÉTRIX (*Bull. Soc. Chim.* [3], **9**, 115—117).—*Triacetyldibromogallic acid*, $\text{C}_6\text{Br}_2(\text{OAc})_3\cdot\text{COOH}$, is prepared by heating dibromogallic acid with acetic chloride; it is amorphous, melts at $94\text{--}95^\circ$, and gives a rose coloration with baryta water or lime water. The *tribenzoyl derivative*, $\text{C}_6\text{Br}_2(\text{OBz})_3\cdot\text{COOH}$, is obtained in a similar manner to the preceding compound, which it closely resembles. It can be purified by dissolving it in ether, and precipitating with water; it melts at $95\text{--}96^\circ$, and gives a green coloration with ferric chloride. Nachbaur's tetracetyl gallic acid and Priwoznik's tetracetyldibromogallic acid, both of which compounds are described in Beilstein's Dictionary, thus appear to have been erroneously analysed and classified.

J. B. T.

Basic Gallate of Bismuth (Dermatol). By H. CAUSSE (*Compt. rend.*, **117**, 232—234).—*Basic bismuth gallate* was obtained by Fischer as a yellow powder, but it may be obtained in crystalline form by precipitating a solution of bismuth nitrate with gallic acid in the

presence of potassium nitrate and acetic acid. It forms small, lemon-yellow crystals, having the composition represented by the formula $C_7H_3O_5Bi \cdot 2H_2O$, is unstable towards air and light, and dissolves readily in strong acids. *Bismuth pyrogallol*, $C_6H_3O_3Bi$, obtained by mixing acetic acid solutions of bismuth oxide and pyrogallol, forms similar yellow crystals. To determine whether the gallate is a phenolic compound, triacetyl gallic acid was treated with bismuth oxide in acetic acid solution. A white powder of *basic bismuth triacetyl gallate*, $C_7H_3Ac_3O_2 \cdot BiO \cdot H_2O$, was obtained, and was also prepared by another method in dehydrated, colourless crystals. A *double gallate of bismuth and magnesium*, $C_7H_2MgBiO_5$, was also prepared; it forms yellow crystals, unstable towards air and light. In consideration of these facts, the constitutional formula of the basic gallate of bismuth is, probably,



JN. W.

Action of Caustic Alkalis on Phthalides. By P. GUCCI (*Gazzetta*, 23, i, 319—322).—On heating dimethylphthalide with soda at about 250° , acetone distils and sodium benzoate remains. Knorr states (*Annalen*, 248, 59) that on heating dimethylphthalide at 100° with potash, potassium hydroxypropylbenzoate is formed; it would thus seem that, on further heating, this salt breaks up into potassium benzoate and acetone. On heating phthalide itself with soda, hydrogen is evolved, and sodium phthalate remains.

W. J. P.

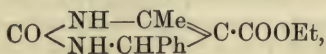
Rotatory Power of Salts of Quinic acid. By S. G. CERKEZ (*Compt. rend.*, 117, 173—177).—The rotatory power of metallic quinates in aqueous solution, has been determined by Hesse (*Annalen*, 176, 124) and Oudemans (*Rec. Trav. Chim.*, 5, 169). The present series of determinations refers to metallic and alkylic quinates in alcoholic solution and to quinates of nitrogenous bases in both alcoholic and aqueous solutions. The results are as follows.

Metallic salts (in 98.5 p. c. alcohol).						
	Li.	Am.	Na.	K.		
$[\alpha]_D$	-15.2	-14.7	-13.6	-7.2		
Alkylic salts (in 95 per cent. alcohol).						
	Me.	Et.	Pr α .	Pr β .	CH $_2$ Pr β .	Ph.
$[\alpha]_D$	-28.6	-26.4	-26.4	-27.6	-26.2	-24.7
Salts of nitrogenous bases.						
	In water.	In 95 p. c. alcohol.		In 98.5 p. c. alcohol.		
	$[\alpha]_D$.	$[\alpha]_D$.		$[\alpha]_D$.		
Diethylamine ...	-31.8	-12.4		-14.3		
Pyridine.....	-30.0	-25.1		-27.1		
Aniline	-28.5	-22.9		-27.6		
Quinoline	-27.4	-22.3		-22.6		

Consideration of these figures shows that the introduction of alkylic radicles and metals diminishes the rotatory power to a considerable extent, whilst that of nitrogenous radicles diminishes it to a less extent, except in the case of diethylamine, the rotatory power of the salt of which is nearly the same as that of the metallic salts. Comparing the rotatory powers of the various salts with those calculated by Oudemans' method, on the amount of quinic acid which would be in solution if the dissociations were complete, it is seen that the alkylic, the metallic, and the diethylamine salts are little dissociated in alcoholic solution, whilst those of the other nitrogenous bases are dissociated to a considerable extent. The values calculated from aqueous solutions of the metallic quinate and from those of the nitrogenous bases are not identical, a result confirming that which might be predicted by the electrolytic dissociation theory. JN. W.

Aldureïdes of Ethylic Acetoacetate and Ethylic Oxalacetate.

By P. BIGINELLI (*Gazzetta*, 23, i, 360—416; compare Abstr., 1891, 908; 1892, 56).—*Ethylic benzuramidocrotonate*,

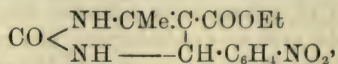


may be prepared by several methods—by heating ethylic acetoacetate or ethylic β -uramidocrotonate with benzaldehyde in alcoholic solution, by boiling an alcoholic solution of ethylic acetoacetate with benzyldiureïde, or by heating ethylic benzalacetoacetate with alcohol and carbamide after acidifying with hydrochloric acid. It forms white laminae melting at 207—208°, or slender needles melting at 206—206·5°; the latter become slowly converted into the former modification when left in contact with the alcoholic mother liquor. It is slowly hydrolysed by water and dilute acids or alkalis, but, on boiling with potash, it yields benzaldehyde, benzylic alcohol, ammonia, and potassium carbonate in addition to a substance, or mixture, containing nitrogen, which is obtained as a yellow, crystalline powder, blackening at 194—196°. On heating the crotonate with concentrated alcoholic potash, a small quantity of acicular crystals, melting at 150—151°, is obtained; the salt is not acted on by nitrous acid.

Ethylic benzuramidobutyrate, $\text{CO} < \begin{array}{c} \text{NH} \cdot \text{CHMe} \\ \text{NH} \cdot \text{CHPh} \end{array} > \text{CH} \cdot \text{COOEt}$, is obtained by reducing the preceding salt with sodium amalgam in alcoholic solution. It forms small needles, melting at 229—230° with decomposition, and is accompanied by a substance obtained as a glassy mass, melting at 59—60°; this is probably a mixture of the compound melting at 229—230° with an isomeride.

A mixture of metanitrobenzaldehyde, ethylic acetoacetate, and carbamide, when heated in alcoholic solution, yields metanitrobenzylidenediureïde and ethylic metanitrobenzalacetoacetate, together with *metanitrobenzylideneureïde*, $\text{CO} < \begin{array}{c} \text{NH} \\ \text{NH} \end{array} > \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$; the latter separates from alcohol as an oil, and is ultimately obtained as a straw-

yellow powder, which melts at about 170° . The mother liquor, on concentration, yields *ethylic metanitrobenzuramidocrotonate*,



which crystallises in beautiful, yellow, monosymmetric prisms, $a : b : c = 0.729 : 1 : 0.1629$; $\beta = 84^{\circ} 7\frac{1}{2}'$, melting at $231\text{--}232^{\circ}$. It is not attacked by ammonium sulphide in hot alcoholic solution.

Cuminaldiureide, $\text{C}_6\text{H}_5\text{MePr}^{\alpha}(\text{NH} \cdot \text{CO} \cdot \text{NH}_2)_2$, is obtained by heating a dilute alcoholic solution of cuminaldehyde and carbamide; it is a white, crystalline powder, melts at $175\text{--}176^{\circ}$, and is sparingly soluble in ether. On treatment with ethylic acetoacetate, it yields *ethylic cuminaluramidocrotonate*, $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}$, which crystallises in small, colourless needles; and melts at $161\text{--}162^{\circ}$; if left in contact with the alcoholic mother liquor for a few days, they change to monosymmetric prisms, $a : b : c = 1.3514 : 1 : 1.4265$; $\beta = 89^{\circ} 24'$, which melt at $164\text{--}165^{\circ}$; the rise in melting point is also brought about by fusion.

Ethylic salicyluramidocrotonate, $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_4$, prepared in a similar manner to the analogous compounds described above, crystallises in white needles melting at $199\text{--}200^{\circ}$, or in a more stable form as monosymmetric prisms, $a : b : c = 1.332 : 1 : 1.075$; $\beta = 56^{\circ} 55'$, which melt at $203\text{--}204^{\circ}$. On passing a current of carbonic anhydride through its solution in alcoholic alkalis, and subsequently adding hydrochloric acid, a substance which seems to have the constitution

$\text{CO} < \begin{array}{c} \text{NH} \cdot \text{CHMe} \cdot \text{CH} \cdot \text{O} \\ \text{NH} \text{ --- } \text{CH} \cdot \text{C}_6\text{H}_4 \end{array}$ separates; it forms lustrous laminae, which decompose at 285° . When heated with dilute sulphuric acid, it yields salicylaldehyde.

Bromine acts on ethylic benzuramidocrotonate in carbon bisulphide solution, yielding a *dibromo-derivative*, $\text{C}_{14}\text{H}_{16}\text{Br}_2\text{N}_2\text{O}_3(?)$, which forms yellow prisms, decomposing at about 173° ; it evolves hydrogen bromide continuously, and hence does not give satisfactory numbers on analysis. Under similar conditions, ethylic salicyluramidocrotonate tends to form a *dibromo-derivative*; on treating it with water, however, hydrogen bromide is given off, and a *monobromo-derivative*, $\text{C}_{11}\text{H}_{11}\text{BrN}_2\text{O}_3$, is obtained in colourless needles melting at $192\text{--}193^{\circ}$.

The action of carbamide on cinnamaldehyde results in the formation of the following compounds, either of which may become the principal product of the reaction if the conditions be varied. *Cinnamaldiureide*, $\text{CHPh} \cdot \text{CH} \cdot \text{CH}(\text{NH} \cdot \text{CO} \cdot \text{NH}_2)_2$, is obtained as a white, crystalline powder, melting at $171\text{--}172^{\circ}$, with decomposition.

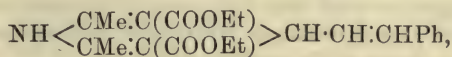
Tricinnamaltetraureide, $\text{C}_9\text{H}_8(\text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2)_2$, forms a crystalline powder melting at $182\text{--}184^{\circ}$ with decomposition. Both the above substances yield cinnamaldehyde and carbamide on boiling with water, alcohol, or acids.

Cinnamalureide, $\text{CO} < \begin{array}{c} \text{NH} \\ \text{NH} \end{array} > \text{NH} \cdot \text{CH} \cdot \text{CHPh}$, is obtained as a porcelain-like mass, melting at about $115\text{--}116^{\circ}$. It behaves similarly to the two ureides described above, but absorbs bromine, which they

do not, and, on boiling with alcohol, yields tricinnamaltetraureide. In addition to the above, a *ureide*, melting at 212° , and a substance crystallising in small needles melting at 220° , are obtained in the reaction between carbamide and cinnamaldehyde.

Ethylic cinnamaluramidocrotonate, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CMe} \cdot \text{C} \cdot \text{COOEt} \\ \text{NH} \text{---} \text{CH} \cdot \text{CH} \cdot \text{CHPh} \end{smallmatrix}$, is prepared by boiling either of the cinnamalureides with ethylic acetoacetate or, more directly, by heating carbamide, cinnamaldehyde, and ethylic acetoacetate in alcoholic solution. It is obtained as thin, white needles, melting at $243\text{--}244^{\circ}$, and absorbs bromine; the compounds thus obtained, however, could not be isolated.

Ethylic benzylidenedihydrocollidinedicarboxylate,



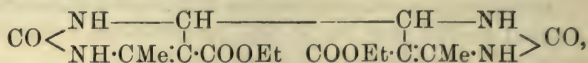
is obtained, together with the preceding compound, on boiling tricinnamaltetraureide with ethylic acetoacetate and a little alcohol; it forms yellow, transparent, monosymmetric prisms, $a : b : c = 1.9270 : 1 : 2.5607$; $\beta = 72^{\circ} 39'$, which melt at $151\text{--}152^{\circ}$. It seems to be isomeric with a substance described by Epstein (*Annalen*, **231**). On treatment with nitrogen trioxide in alcoholic solution, then saturating with carbonic anhydride, and adding hydrochloric acid, a *benzylidenecollidinedicarboxylic acid hydrochloride* is obtained in needles, which decompose at about 120° . This substance gives off hydrogen chloride on exposure to the air, and, on heating with water, yields an *acid*, which crystallises in prisms melting at 156° ; the acid obtained by Epstein from his hydrochloride melted at $218\text{--}219^{\circ}$.

Difurfuraltriureide, $\text{CO}[\text{NH} \cdot \text{CH}(\text{C}_4\text{OH}_3) \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2]_2$, is obtained by the action of carbamide on furfuraldehyde; it forms a white powder, which melts at $168\text{--}169^{\circ}$, and is insoluble in hot alcohol. It is accompanied by a small proportion of another *ureide*, which melts at $171\text{--}172^{\circ}$, and is very soluble in alcohol. On boiling the triureide with ethylic acetoacetate, it yields ethylic β -uramidocrotonate and *ethylic furfuramidocrotonate*; the latter forms yellowish, anorthic prisms, $a : b = 2.096 : 1$; $\alpha = 76^{\circ} 9'$, $\beta = 80^{\circ} 41'$, $\gamma = 64^{\circ} 55'$, or leaflets melting at $208\text{--}209^{\circ}$.

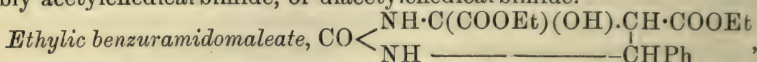
Ethylic formuramidocrotonate, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CMe} \\ \text{NH} \cdot \text{CH}_2 \end{smallmatrix} > \text{C} \cdot \text{COOEt}$, is prepared by heating methenylcarbimide with ethylic acetoacetate dissolved in alcohol; it forms minute needles melting at $260\text{--}261^{\circ}$, and is soluble in alcohol.

On heating acetaldehyde, ethylic acetoacetate, and carbamide in alcoholic solution, a substance of the composition $\text{C}_{15}\text{H}_{32}\text{N}_8\text{O}_5$ is obtained as a white powder melting at 184° , with decomposition; *ethylic aceturamidocrotonate*, $\text{CO} \begin{smallmatrix} \text{NH} \text{---} \text{CMe} \\ \text{NH} \cdot \text{CHMe} \end{smallmatrix} > \text{C} \cdot \text{COOEt}$, is also formed; this crystallises in anorthic prisms, $a : b : c = 1.1561 : 1 : 0.9112$; $\alpha = 59^{\circ} 5'$, $\beta = 90^{\circ} 51'$, $\gamma = 80^{\circ} 55'$, melts at $195\text{--}196^{\circ}$, and is soluble in alcohol.

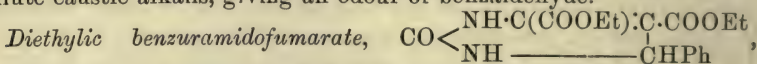
Ethylic acetylenediuramidocrotonate,



is prepared by heating ethylic acetoacetate, glyoxal, and carbamide in alcoholic solution; it forms white, monosymmetric laminae, $a : b : c = 2.2723 : 1 : 1.2020$; $\beta = 75^\circ 42'$, melts at 139° , and is soluble in most organic solvents. It is accompanied by another substance, $(\text{C}_3\text{H}_2\text{N}_2\text{O})_x$, which forms needles melting at $152\text{--}154^\circ$; this is possibly acetylenedicarbimide, or diacetylenedicarbimide.

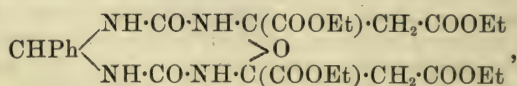


is obtained, together with the following compound, by digesting a mixture of ethylic oxalacetate, benzaldehyde, and carbamide in alcoholic solution; it forms white needles, which melt at 183° , with decomposition. It is not attacked by bromine, but dissolves readily in dilute caustic alkalis, giving an odour of benzaldehyde.



forms white, orthorhombic prisms, showing sphenoidal hemihedrism, $a : b : c = 0.8451 : 1 : 0.4607$, and melting at $176\text{--}177^\circ$; it seems to be accompanied by an isomeride which melts at 179° .

Tetrethylic benzodiuramidodimaleate,



is obtained by treating ethylic benzuramidomaleate with caustic alkali; it separates from its solution in prisms melting at $156\text{--}157^\circ$, and is very soluble in alcohol.

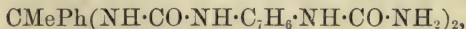
On adding hydrochloric acid to a solution of either of the three preceding substances in caustic alkali, *ethylic hydrogen benzuramidofumarate*, $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_5$, is obtained; it forms prismatic crystals which decompose at $220\text{--}230^\circ$. Its *silver* salt, $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_5\text{Ag}$, melts at 217° with decomposition. *Ethylic methylic benzuramidofumarate* forms white needles which soften at 187° . The ethylic hydrogen salt seems to be accompanied by an isomeride, which is less soluble, and more stable towards heat.

Ethylic hydrogen benzuramidosuccinate, $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_5$, is prepared by reducing the corresponding fumarate (which decomposes at $220\text{--}230^\circ$) with sodium amalgam; it crystallises in needles, melts at $224\text{--}225^\circ$, is not acted on by bromine, and is reprecipitated by hydrochloric acid from its solutions in alkali carbonates.

On heating an alcoholic solution of acetone, carbamide, and benzaldehyde, a white substance, $\text{C}_{19}\text{H}_{24}\text{N}_6\text{O}_4$, is obtained, melting at $186\text{--}187^\circ$; also another compound, $\text{C}_{25}\text{H}_{30}\text{N}_6\text{O}_5$, as a white powder melting at $182\text{--}183^\circ$ with decomposition. If a little hydrochloric acid is added to an alcoholic solution of acetone, carbamide, and benzaldehyde, and the mixture kept for two months, a substance which blackens at 280° is obtained, together with a compound of the

composition $C_{27}H_{30}N_6O_4$, which crystallises with alcohol in white needles melting at 270° with decomposition. The latter, on heating with methylic iodide, gives a compound containing iodine, which crystallises in yellow needles decomposing at 220 — 221° .

Dibenzoacetophenonetetraureide,



is obtained by heating an alcoholic solution of acetophenone, benzaldehyde, and carbamide; it is a white powder, which decomposes at 176 — 180° .

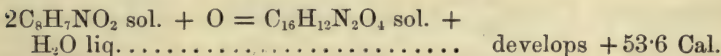
The interaction of benzaldehyde, carbamide, and ethylic ethyl-acetoacetate yields a *substance* of the composition $C_{26}H_{36}N_8O_6$, which decomposes at 181 — 183° , and during purification loses benzaldehyde and carbamide, giving a *compound*, $C_{15}H_{18}N_4O_3$, which decomposes at 190 — 191° .

W. J. P.

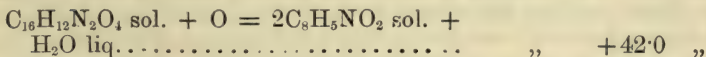
Heat of Formation of some Derivatives of Indigotin. By R. D'ALADERN (*Compt. rend.*, **116**, 1457—1459).—The determinations were made with a calorimetric bomb.

	Heat of combustion.		Heat of formation.
	At constant volume.	At constant pressure.	
Indigotin, $C_{16}H_{10}N_2O_2$	1815·2	1812·6	+ 41·0 Cal.
Isatin, $C_8H_5NO_2$	867·4	867·8	+ 59·0 „
Isatide, $C_{16}H_{12}N_2O_4$	1777·3	1777·8	+ 145·0 „
Dioxindole, $C_8H_7NO_2$	915·3	915·7	+ 80·2 „

From these results it follows that



and



The very considerable development of heat explains the ready oxidation of dioxindole by simple exposure to air. C. H. B.

Acridone. By C. GRAEBE and K. LAGODZINSKI (*Annalen*, **276**, 35—53).—The preparation of acridone from phenylanthranilic acid has been already described (*Abstr.*, 1892, 1086). In the present communication, the authors give their experiments in detail, and correct certain misstatements. They were unable to prepare acridone directly from anthranilic acid by a method similar to that employed for the preparation of xanthone from salicylic acid. Pictet and Hubert (*Arch. Sci. phys. nat.*, 1893, 215) have, however, observed that acridone is formed when salicylanilide is strongly heated; they believe that phenylanthranilic acid is an intermediate product.

The preparation of phenylanthranilic acid (*loc. cit.*) is effected from 1 : 3 : 6-amidophenylanthranilic acid, and the compound now employed by the authors as the starting point is orthochlorobenzoic acid, instead of orthobromobenzoic acid. Orthochlorobenzoic acid (this vol., i, 641) is nitrated by boiling it with nitric acid of 1.48 sp. gr., the nitro-acid heated at 170—175° with aniline, and the product reduced with tin and hydrochloric acid. 1 : 3 : 6-*Amidophenylanthranilic acid* is a colourless compound, insoluble in water; it melts at 233—234° with decomposition, yielding chiefly paramidodiphenylamine. The *hydrochloride* crystallises in bright yellow needles, and dissociates when boiled with water; the *stannochloride* also crystallises in yellow needles.

Phenylanthranilic acid is prepared by treating amidophenylanthranilic acid dissolved in alcoholic hydrochloric acid with sodium nitrite at 20—25°, pouring the liquid into a solution of stannous chloride in hydrochloric acid, and precipitating the phenylanthranilic acid with water. The acid decomposes when distilled, yielding principally diphenylamine, but also traces of acridone.

Acridone is prepared as already described (*loc. cit.*); it melts at 354° (corr.), and, like xanthone, forms neither a hydrazone nor an oxime. The methylacridone described by Decker (Abstr., 1892, 881) is obtained by heating a mixture of acridone and potassium hydroxide, moistened with alcohol, at 160—170°, and subsequently heating the pulverised melt with methylic iodide in a sealed tube at 130—140; it melts at 203.5° (corr.), not at 190° (*loc. cit.*). *Ethylacridone*, $C_6H_4 < \begin{smallmatrix} CO- \\ NEt \end{smallmatrix} > C_6H_4$, melts at 159° (corr.). Acridone is readily converted into acridine when it is heated with zinc-dust, treated with sodium amalgam, or fused with potassium cyanide.

Chloracridine, $C_6H_4 < \begin{smallmatrix} CCl \\ N \end{smallmatrix} > C_6H_4$, is obtained by heating acridone at 120—130° with phosphorus pentachloride and some phosphorus oxychloride; it crystallises in colourless needles, melts at 119° (corr.), and sublimes readily; the vapour irritates the mucous membrane, and the compound attacks the skin in the same manner as acridine. On being boiled with water, a portion volatilises, but the greater part is converted into acridone (the latter reaction is exhibited also by its salts), probably through the intermediary formation of the unstable *acridol*, $C_6H_4 < \begin{smallmatrix} C(OH) \\ N \end{smallmatrix} > C_6H_4$. The *hydrochloride* forms long, yellow needles, very soluble in water, and the *picrate* is sparingly soluble in water, and melts above 330°.

To settle the nature of the product which Graebe and Caro obtained (Abstr., 1880, 399) by oxidising acridine, this substance was gently boiled with sodium dichromate and glacial acetic acid; it is found that acridone is first formed, and on continuing the oxidation it is converted into *biacridonyl*, $CO < \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} > N \cdot N < \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} > CO$, together with acridinic acid. *Biacridonyl* is also obtained by oxidising ready-formed acridone; it melts at 251°, and, unlike acridone, its solutions

do not exhibit fluorescence, and it is insoluble in alcoholic alkalis. On being heated with zinc-dust, acridine is formed, and hydracrydine is obtained when it is warmed with sodium amalgam. In support of the above constitutional formula, it is urged that methylacridone, when it is oxidised as above, is only with difficulty converted into biacridonyl.

A. R. L.

Dichloronaphthalene. By H. ERDMANN (*Annalen*, 275, 255—261).—1:3'-Dichloronaphthalene melts at 48° , the 1:2'-isomeride at 62.5° , and the 1:3- at 61° ; the former is readily characterised by its melting point, whilst the other two are distinguished from each other by their nitration products. The 1:2'-compound gives a mononitro-derivative melting at $138-139^{\circ}$, whilst the 1:3-isomeride under similar conditions yields a dinitro-derivative melting at 240° .

W. J. P.

Separation and Constitution of Isomeric Naphthalene Derivatives. By H. ERDMANN (*Annalen*, 275, 184—191).—The author comments on the difficulty of separating isomeric naphthalene derivatives; a direct separation of neutral isomerides is, as a rule, impossible; recourse must be had to the strongly acid sulphonic derivatives. The salts of the sulphonic acids may often be separated with ease by the use of methyl and ethyl alcohols as solvents. In addition to the well-known prefixes, ortho, meta, para, and peri, the author introduces several others, which he thinks will facilitate the description of the isomeric di-derivatives of naphthalene, thus:—*ana* = 1:4'; *epi* = 1:3'; *kata* = 1:2'; *amphi* = 2:3'; *pros* = 2:2'.

As the double bonds in the naphthalene symbol can be arranged in three different ways, the author considers it possible that three geometrical isomerides of the $\alpha\beta$ -heteronuclear di-derivatives of naphthalene may exist; it is, in his opinion, significant that the 1:2'-naphthylaminesulphonic acid may be obtained in three forms, containing different quantities of water of crystallisation.

W. J. P.

Isomeric α -Mononitronaphthalenemonosulphonic acids. By H. ERDMANN and C. SÜVERN (*Annalen*, 275, 230—254).—By the nitration of α -naphthalenesulphonic chloride below 3° , a mixture of 1:4'- and 1:1'-nitronaphthalenesulphonic chlorides is obtained; the product is poured on to ice, washed, and dried. The 1:4'-sulphonic chloride is separated from the mass by extraction with boiling carbon bisulphide in a specially devised apparatus, whilst the 1:1'-isomeride remains undissolved, and is purified by crystallisation from chloroform.

1:1'-Nitronaphthalenesulphonic chloride forms fine, colourless prisms, which decompose with evolution of gas at 161° ; it is sparingly soluble in ether, light petroleum, or carbon bisulphide, but dissolves readily in most other organic solvents. It is easily hydrolysed by heating with aqueous bases, but does not yield the acid in a pure state when heated with water in a sealed tube. The sulphonic acid is obtained by heating its methyl salt with water at 130° ; it is readily soluble in water, and separates from the solution in brilliant, yellow needles containing $3H_2O$, of which it retains $1\frac{1}{2}$ at 100° , and $\frac{1}{3}$ in a vacuum

over sulphuric acid. It cannot be obtained anhydrous, and is soluble in alcohol and ether; on reduction, it yields the corresponding amido-acid (Abstr., 1889, 156). The *potassium* salt forms yellow plates, containing $2\frac{1}{2}\text{H}_2\text{O}$, or asbestos-like needles with $1\text{H}_2\text{O}$. The *ammonium* salt with $2\text{H}_2\text{O}$ forms brown, hard plates, and explodes at 210° . The *calcium* salt crystallises with $4\frac{1}{2}\text{H}_2\text{O}$ in brilliant, yellow plates, and is soluble in water or alcohol, but insoluble in ether; the *barium* salt with $2\frac{1}{2}\text{H}_2\text{O}$, and the *zinc* salt with $9\text{H}_2\text{O}$, form hard, brown prisms. The *silver* salt is unstable, separates from its aqueous solution in yellow, anhydrous needles, and is soluble in alcohol. The *sulphonamide* forms white, monosymmetric prisms melting at 185° ; it is soluble in chloroform, methyl alcohol, acetone, and acetic acid. The *anilide* is obtained in colourless needles melting at 173° . The *methylic* salt is prepared by heating the sulphonic chloride with methyl alcohol and sodium methoxide; it forms transparent prisms melting at 124° . It is soluble in benzene, and in warm methyl or ethyl alcohol, but only sparingly in chloroform. It is only slowly hydrolysed by heating with water. The *ethylic* salt is prepared by an analogous process, and forms colourless prisms melting at 118° ; it is soluble in chloroform.

With the exception of one or two unimportant details, the authors confirm Cleve's description of the 1:4'-nitronaphthalenesulphonic acid and its derivatives; the *methyl* salt melts at 117.5° .

A *dinitronaphthalenesulphonic chloride* is also separated from the product of nitrating α -naphthalenesulphonic chloride; it forms large, transparent prisms, which decompose at 117° on rapid heating.

The nitration of β -naphthalenesulphonic chloride yields 1:2'- and 1:3'- α -nitronaphthalenesulphonic chlorides. W. J. P.

Perinitronaphthalenesulphonic acid. By H. ERDMANN and C. SÜVERN (*Annalen*, 275, 305—309; compare Limpricht, Abstr., 1892, 475).—On heating perinitronaphthalenesulphonic chloride with a solution of potassium hydrogen sulphite and carbonate, perinitronaphthalenesulphonic acid, $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_2\text{H}$, is formed. Its *paratoluidine* salt forms minute, yellow needles; the *barium* salt separates in small, brilliant scales containing $6\text{H}_2\text{O}$, whilst the *potassium* salt forms yellow scales with $2\text{H}_2\text{O}$. On distilling the salts with sulphuric acid in a current of steam, α -nitronaphthalene passes over. W. J. P.

Derivatives of 3':1-Acetonaphthol. By H. ERDMANN and F. HENKE (*Annalen*, 275, 291—296; compare Abstr., 1890, 375).—Pure 3':1-acetonaphthol is best obtained by heating its oxime with hydrochloric acid; it melts at 173 — 174° . On heating it with benzaldehyde and caustic soda, it yields *benzalacetosodionaphthol*, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_{10}\text{H}_6\cdot\text{ONa}$, which crystallises in dark prisms containing $5\text{H}_2\text{O}$, and absorbs carbonic anhydride from the air. It is very unstable, and, on passing carbonic anhydride through its aqueous solution, *benzalacetone* is deposited as a yellow, amorphous powder, which readily decomposes, giving benzaldehyde.

Acetonaphthol yields a *monobromo*-derivative in beautiful needles melting at 149° , and a *dibromo*-derivative melting at 124 — 125° ; a

pentabromo-derivative is also obtained in yellow flocks, soluble in carbon bisulphide, benzene, alcohol, or chloroform.

The ethoxy-derivative of acetonephthol gives a *pentabromo*-derivative, $C_{14}H_7Br_5O_3$; it forms large, colourless prisms melting at $110-111.5^\circ$. Acetonephthol readily gives *dinitracetonephthol* in brilliant, yellow scales which melt at $145-146^\circ$ with decomposition.

W. J. P.

Compounds of Substituted Naphthalenesulphonic acids with Organic Bases. By H. ERDMANN and C. SÜVERN (*Annalen*, 275, 297—305).—The salts of the substituted naphthalenesulphonic acids with organic bases are mostly sparingly soluble, stable compounds, and are hence applicable to the isolation of readily soluble sulphonic acids. The authors have examined a number of these salts.

W. J. P.

Synthetical Tri-derivatives of Naphthalene. By H. ERDMANN and E. SCHWECHTEN (*Annalen*, 275, 283—291; compare Abstr., 1891, 448).—On heating orthoparadichlorophenylparaconic acid, it loses carbonic anhydride, giving the corresponding isocrotonic acid; on further heating, water distils off, carrying with it 2':4':1-*dichloronaphthol*. This substance forms large, yellow prisms melting at 132° , is soluble in carbon bisulphide or hot water, and gives naphthalene on distillation with zinc dust. Its *monacetyl* derivative melts at 110° . On heating the dichloronaphthol with aqueous ammonia at $150-200^\circ$, 2':4':1-*dichloronaphthylamine* is obtained; it crystallises in microscopic needles melting at $116-117^\circ$. The *hydrochloride* forms white crystals melting at $204-205^\circ$, and is decomposed by water.

Paradichlorophenylparaconic acid gives only a small yield of 1':4':1-*dichloronaphthol* when distilled; the latter melts at $114-115^\circ$, and is sparingly soluble in hot water. Its *monacetyl* derivative crystallises in large, yellow prisms which melt at $144-145^\circ$. The naphthol is converted into 1':4':1-*dichloronaphthylamine* by heating it with aqueous ammonia at 300° ; this base crystallises in white scales, melts at $68-69^\circ$, and gives a *hydrochloride* which decomposes at 230° .

On heating, 3:4:1-dichlorophenylisocrotonic acid yields two isomeric *dichloronaphthols*, which can be separated by means of light petroleum. One of these melts at $149-150^\circ$, and gives a *monacetyl* derivative crystallising in white needles and melting at $102-103^\circ$; on oxidation with chromic mixture, it yields a *dichlorophthalic acid*, which crystallises in small, white needles containing $1H_2O$, and melts at $189-190^\circ$. The other dichloronaphthol forms microscopic needles melting at $83-84^\circ$, and gives a *monacetyl* derivative which crystallises in small, white needles melting at $71-72^\circ$.

W. J. P.

Sulphonation of α -Naphthylamine. By H. ERDMANN (*Annalen*, 275, 192—224).—The author disputes the validity of Armstrong and Wynne's explanation (Proc., 1889, 5) of the mixture of isomerides obtained during the sulphonation of, say, α -naphthylamine, on the basis of isomeric change; on sulphonation at 130° , naphthionic acid is the first product, but as time goes on the melt becomes richer and richer in the isomeric 1:4'- and 1:3'-acids.

Naphthionic acid in contact with hot sulphuric acid readily gives α -naphthylamine; the 1 : 4'-acid decomposes with much less readiness, whilst the 1 : 3'-acid is very stable under such conditions. By continued decomposition of the sulphonic acids at different rates and simultaneous re-sulphonation of the α -naphthylamine, the proportion of the more stable 1 : 4'- and 1 : 3'-acids would continually increase; that α -naphthylamine is always present is shown by the fact that a portion of the melt taken when it is completely soluble in alkali always yields the amine on extraction with ether. The quantity of free α -naphthylamine increases with the time of heating owing to the formation of Dahl's disulphonic acid III. The explanation given above is supported by the results of a series of experiments on the speed of hydrolysis of the various sulphonic acids.

α -Naphthylamine (400 grams), on sulphonation at 125—130° for 22 hours with 95—96 per cent. sulphuric acid (2 kilos.), and subsequent conversion of the product into calcium salt, yields a mixture of calcium 1 : 4'-naphthylaminesulphonate (140—160 grams) and calcium 1 : 3'-naphthylaminesulphonate. The salt of the 1 : 4'-acid is partially separated by crystallisation, and the residue obtained on evaporating the mother liquor to dryness is completely freed from this salt by extraction with absolute alcohol. The salt of the disulphonic acid is then removed by extraction with cold methyl alcohol; the residue, when dissolved in water and acidified, yields the 1 : 3'-acid (55 grams). The calcium salt of the 1 : 4'-acid thus obtained contains a little calcium naphthionate, which may be removed by taking advantage of the fact that the sodium salt of the former acid is soluble in absolute alcohol, whilst sodium naphthionate is only very sparingly soluble.

1 : 3'-Naphthylaminesulphonic acid separates, on acidifying its hot alkaline solution, in white needles changing to compact, brilliant, anhydrous cubes; cooler solutions yield the acid in large, thin leaves containing $2\text{H}_2\text{O}$. Dilute solutions give a brilliant blue coloration with ferric chloride, and a violet with gold chloride; the acid is sparingly soluble in water. The *sodium* salt forms crystalline crusts containing $1\text{H}_2\text{O}$; it is soluble in cold methyl alcohol, but only very sparingly so in hot ethyl alcohol. The *potassium* salt, with $1\text{H}_2\text{O}$, is obtained in large, white crystals, soluble in water, but insoluble in alcohol. The *calcium* salt crystallises in rhomboïdal plates with $7\text{H}_2\text{O}$ or in small crystals with $2\text{H}_2\text{O}$; it dissolves readily in water, but is almost insoluble in methyl or ethyl alcohol. The *magnesium* and *zinc* salts form large, rhomboïdal tables containing $12\text{H}_2\text{O}$; the *cadmium* salt crystallises with $4\text{H}_2\text{O}$ in small rhombohedra, or in needles containing $8\text{H}_2\text{O}$. The *silver* salt forms well-defined prisms. 1 : 3'-Diazonaphthalenesulphonic acid is obtained by diazotising the potassium salt described above; it forms small crystals which decompose at 94°. On heating it with a mixture of phosphorus tri- and penta-chlorides, it yields the 1 : 3'-dichloronaphthalene; the constitution of the acid is thus determined.

The small proportion of disulphonic acids produced in the sulphonation consists principally of Dahl's α -naphthylaminedisulphonic acid III. The *potassium* salt, $\text{NH}_2\cdot\text{C}_{10}\text{H}_5(\text{SO}_3\text{K})_2\cdot\frac{2}{3}\text{H}_2\text{O}$, forms large,

augite-like crystals, and is sparingly soluble in water. The author's experiments indicate that Dahl's α -naphthylaminedisulphonic acid I has no existence.

On sulphonating α -naphthylamine in large quantities for technical purposes, a very small proportion of the so-called ν -naphthylamine-sulphonic acid is obtained. The *calcium* salt with $10\text{H}_2\text{O}$ is soluble in methyl alcohol and water, but is distinguished from the corresponding salt of the 1 : 4'-acid by its very sparing solubility in ethyl alcohol. The free acid forms silky needles, and yields a sparingly soluble *diazo*-compound which gives a bluish-red colour with α -naphthol in alkaline solution. This acid is not obtained in the sulphonation of pure α -naphthylamine. The mother liquor, after separating the calcium salt of this acid, contains a small quantity of the salt of a very sparingly soluble *disulphonic acid*; this is probably derived from β -naphthylamine, and is provisionally termed the ξ -acid. Its *calcium* salt with $5\text{H}_2\text{O}$ forms slightly coloured needles, is very soluble in water or methyl alcohol, but insoluble in ethyl alcohol. Its aqueous solution is at first unaltered by the addition of ferric chloride, but after a few minutes it acquires a chocolate colour and the solution becomes turbid. With β -naphthol, the *diazo*-compound of this acid gives a bluish-red colouring matter which may be salted out.

W. J. P.

Synopsis of the Naphthylaminesulphonic acids. By H. ERDMANN (*Annalen*, 275, 262—282).—The author gives the physical properties, such as solubility, electrical conductivity (Ebersbach, this vol., ii, 451), and heat of combustion, of the seven known naphthylaminesulphonic acids; he has also prepared and examined a number of new salts of these acids.

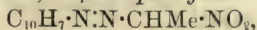
W. J. P.

Behaviour of Sodium or Potassium Naphthionate at High Temperatures. By H. ERDMANN (*Annalen*, 275, 225—230).—Landshoff and Meyer have shown (D. R. Patent, 1890, 56563) that the readily soluble 1 : 2- α -naphthylaminesulphonic acid is formed on heating salts of naphthionic acid at 200—205°. The change from one isomeride to the other is, however, not direct, but decomposition, succeeded by re-sulphonation, occurs. On heating dry sodium naphthionate at 180—220° in a loosely-covered vessel, ammonia, sulphurous anhydride, α -naphthylamine, and a small proportion of volatile colouring matter, soluble in alcohol, are given off, and carbonisation occurs; the residue contains potassium sulphate and salts of disulphonic acids, of the 1 : 2-monosulphonic acid, and of naphthionic acid.

Cleve's statement (*Abstr.*, 1892, 345) that the 1 : 2-acid crystallises with $\frac{1}{2}\text{H}_2\text{O}$ seems to be erroneous; a little water is merely carried down mechanically during separation. The aqueous solution of this acid gives a green precipitate with ferric chloride, and reduces gold chloride.

W. J. P.

Mixed Naphthylazo-compounds. By G. ODDO and G. AMPOLA (*Gazzetta*, 23, i, 257—263).— β -Naphthylazonitroethane,



separates in voluminous, yellow flocks on slowly mixing ice-cold solutions of β -diazonaphthalene chloride and sodionitroethane; it is purified by dissolving in caustic potash and precipitating by hydrochloric acid. It forms lustrous, red scales which melt at 145° with rapid decomposition; it is soluble in alcohol, but only sparingly so in chloroform, benzene, ether, or light petroleum, and has a strawberry-like odour.

β -Naphthylazonitrosoethane, $C_{10}H_7 \cdot N_2 \cdot CMe(NO) \cdot NO_2$, is precipitated on adding hydrochloric acid to a caustic potash solution of the previous compound, to which potassium nitrite has been added; it forms dark red needles melting at 141° , and gives Liebermann's reaction for nitroso-compounds.

β -Naphthylazobromonitroethane, $C_{10}H_7 \cdot N_2 \cdot CMeBr \cdot NO_2$, is obtained by direct bromination in alcoholic solution, and crystallises in yellow scales or needles which melt at 168° with decomposition; it is insoluble in alkalis.

α -Naphthylazonitroethane is obtained in a similar manner to the β -isomeride; the yield is, however, much smaller. It forms dark red scales melting at 105.5 — 106° .

The action of various reducing agents on the β -isomeride was investigated in the hope of obtaining the hitherto unknown ethilidene-diamine; the only products isolated, however, were ammonia and β -naphthylamine.

W. J. P.

Oxygenated Derivatives of Acenaphthene. By C. GRAEBE and E. GFELLER (*Annalen*, 276, 1—20; compare Abstr., 1892, 863).—The so-called acenaphthenequinone (*loc. cit.*) is best prepared by stirring pulverised sodium dichromate (40—45 grams), not too slowly, into a mixture of acenaphthene (10 grams) and glacial acetic acid (70 c.c.) at a temperature of 100° , precipitating with water, and extracting the crude compound with a boiling 40 per cent. solution of sodium hydrogen sulphite. Under these circumstances, the additive compound, $C_{12}H_6O_2 \cdot NaHSO_3 + 2H_2O$, is formed, and when cold sulphuric or hydrochloric acid is added to its aqueous solution, acenaphthenequinone is precipitated. Acenaphthenequinone, like phenanthraquinone, exhibits Laubenheimer's reaction, thus:—When the finely pulverised compound is suspended in glacial acetic acid, (1) on addition of crude toluene and an excess of concentrated sulphuric acid, a dirty green liquid is formed which, when shaken with ether, colours the latter a deep red; (2) on the addition of concentrated sulphuric acid and a drop of thiophen, a dark green liquid is obtained which, when shaken with chloroform, colours it blue or bluish-violet.

When acenaphthenequinone is heated at 100° in a sealed tube with concentrated ammonia, a red compound is obtained which does not melt at 300° , and has, probably, the constitution $(C \begin{array}{c} \diagup N \diagdown \\ \diagdown C_{10}H_6 \diagup \end{array} C)_2O$.

The dioxime, $C_{10}H_6 \begin{array}{c} C:NOH \\ | \\ C:NOH \end{array}$, is a colourless compound melting at

222° with decomposition; the *hydrazone*, $C_{10}H_6 < \begin{smallmatrix} CO \\ C:N_2HPh \end{smallmatrix}$, crystallises in small, orange needles, and melts at 179°; whilst the *dihydrazone*, $C_{10}H_6 < \begin{smallmatrix} C:N_2HPh \\ C:N_2HPh \end{smallmatrix}$, formed by heating the quinone with an excess of phenylhydrazine at 130–140°, crystallises in small, dark yellow needles, and melts at 219°. The authors have qualitatively established that acenaphthenequinone behaves with orthodiamines and with ethylic acetoacetate in a manner similar to phenanthraquinone. Acenaphthenequinone is quantitatively converted into naphthalic acid by warming it with sodium or potassium dichromate and glacial acetic acid or sulphuric acid. It is less readily reduced than phenanthraquinone, and a dihydroxy-derivative (quinol) was not isolated. Sulphurous acid only attacks it at 150°, and biacenaphthylidenediketone (see below) is formed. When the quinone is heated with zinc-dust and acetic acid, various products are obtained, and among them acenaphthenone and acenaphthene.

Acenaphthenone, $C_{10}H_6 < \begin{smallmatrix} CH_2 \\ CO \end{smallmatrix}$, is prepared by adding zinc-dust, in small portions at a time, to a boiling solution of acenaphthenequinone in glacial acetic acid until it is decolorised. It forms colourless leaflets melting at 121°. It dissolves in alcoholic potash, forming a violet solution from which it is reprecipitated unchanged on acidification, but when boiled with sodium hydroxide it is converted into naphthalic acid. The *oxime*, $C_{10}H_6 < \begin{smallmatrix} CH_2 \\ C:NOH \end{smallmatrix}$, forms colourless leaflets, and melts at 175°.

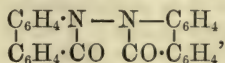
Naphthaldehydic acid (*loc. cit.*) melts at 167–168° (not 172°), and on raising the temperature higher it resolidifies, and melts a second time at 290–295°; the *calcium* salt, $(C_{12}H_7O_3)_2Ca$, is readily soluble in water. Neither the acid nor its salts give a coloration with a magenta solution decolorised by sulphurous acid. Alkaline potassium permanganate converts naphthaldehydic acid into naphthalic acid, whilst nitric acid, or glacial acetic acid and chromates, converts it into naphthalic anhydride. The *acetyl* derivative, $C_{10}H_6 < \begin{smallmatrix} CH(OAc) \\ CO \end{smallmatrix} > O$, melts at 140°, and is hydrolysed by alkalis. The *hydrazone*, $C_{10}H_6 < \begin{smallmatrix} CH(N_2H_2Ph) \\ CH(N_2H_2Ph) \end{smallmatrix} > O$, is obtained by heating an alcoholic solution of naphthaldehydic acid with phenylhydrazine; it melts at 213°. When an alcoholic solution of naphthaldehydic acid is treated with hydroxylamine in molecular proportion, a yellow precipitate separates; this passes, with loss of water, into a more stable compound, $C_{12}H_7NO_2$, which forms small, white needles, and melts at 257°. If, however, an alcoholic solution of naphthaldehydic acid is treated with twice the quantity of hydroxylamine (2 mols.), a compound $C_{12}H_{10}N_2O_3$ is obtained; it crystallises in small, white needles, and melts at 214° with slight decomposition.

Biacenaphthylidenediketone, $C_{10}H_6 < \begin{smallmatrix} CO & CO \\ || & | \\ C = & C - \end{smallmatrix} > C_{10}H_6$ (*loc. cit.*), is

obtained by the incomplete oxidation of acenaphthene with glacial acetic acid and a chromate, and also by heating acenaphthenequinone with dilute hydriodic acid and red phosphorus in a sealed tube at 115—125°; it melts at 295° (corr.). The diketone is not attacked by alkalis; but concentrated sulphuric acid dissolves it with a green colour which changes to red on adding a drop of nitric acid. If the diketone is heated with hydriodic acid and phosphorus at 160—170°, a carbonaceous mass is formed from which a small quantity of acenaphthene may be isolated. The *dibromide*, $C_{24}H_{12}Br_2O_2$, melts at 237°, and the *hydrazone*, $C_{30}H_{18}N_2O$, forms a brownish-red, crystalline powder, and melts at 105—110°.

A. R. L.

Phenanthridone. By C. GRAEBE and C. A. WANDER (*Annalen*, 276, 245—253).—In order to ascertain whether the so-called hydroxyphenanthridine obtained by Pictet and Ankersmit (Abstr., 1892, 196) is identical with Graebe and Aubin's phenanthridone (Abstr., 1889, 145), the authors reduced nitrodiphenylcarboxylic acid, and obtained, besides amido-acids, a small quantity of a compound insoluble in alkalis, identical with phenanthridone (m. p. 293°). However, they subsequently examined a specimen of Pictet and Ankersmit's preparation, and found that it did not give a benzyl derivative, as phenanthridone does (see below). They suggest that the so-called hydroxyphenanthridine may have the constitution



analogous to biacridonyl. Phenanthridone is best prepared by treating an alkaline solution of diphenaminic acid, or of diphenamide, with a hypochlorite or hypobromite, and subsequently with sulphurous acid, and finally precipitating the compound with an excess of dilute sulphuric acid. It is insoluble in aqueous alkalis and dilute acids, but dissolves in alcoholic alkalis; its solutions, unlike those of acridone, do not exhibit fluorescence. It does not form an acetyl derivative, remains unaltered when treated with acetic acid and sodium dichromate, and is converted into the potassium derivative when heated at 300° with potassium hydroxide. When phenanthridone is heated with zinc-dust, phenanthridine is formed; the production of the latter from phenanthrene through diphenaminic acid

takes place in six stages. *Chlorophenanthridine*, $\begin{array}{c} C_6H_4 \cdot CCl \\ C_6H_4 \cdot N \end{array}$, is obtained by heating phenanthridone in a sealed tube at 190° with phosphorus pentachloride; it forms colourless needles, melts at 116·5° (corr.), is soluble in alcohol, and is converted into phenanthridone when heated with lime.

Methylphenanthridone, $\begin{array}{c} C_6H_4 \cdot NMe \\ C_6H_4 \cdot CO \end{array}$, is obtained by heating the potassium derivative of phenanthridone with methylic iodide in a sealed tube at 150—160°; it melts at 108·5° (corr.). The corresponding *ethyl* derivative melts at 89° (corr.), and the *benzyl* derivative at 112·5° (corr.). The authors contend that the foregoing results favour

the view that phenanthridone is a ketonic, and not a hydroxylic, compound. A. R. L.

Dihydroxyanthraquinoneformamides. By PRUD'HOMME and C. RABAUT (*Bull. Soc. Chim.* [3], 9, 131—133).—*Dihydroxyanthraquinone-formamide*, $C_6H_4 \begin{smallmatrix} CO \\ CO \end{smallmatrix} C_6H(OH)_2 \cdot NH \cdot CHO$ [OH : OH : NH = 1 : 2 : 3], is formed on boiling the corresponding dihydroxyamidoanthraquinone with 10 parts of formic acid (70 per cent.), and is a yellow compound giving a violet-blue coloration with alkalis, and a violet-red one with ammonia. It combines with mordants, yielding an orange dye with aluminium, and brown with iron and chromium. On heating with sulphuric acid and glycerol, alizarin-blue is formed, whilst by the action of concentrated alkalis, or of sulphuric acid alone, it is resolved into its constituents. The isomeric formamide [OH : OH : NH = 1 : 2 : 4] is prepared in a similar manner to the preceding compound, which it closely resembles. Towards mordants it behaves like dihydroxyanthraquinone. J. B. T.

Pine Needle Oils. By J. BERTRAM and H. WALBAUM (*Arch. Pharm.*, 231, 290—305).—A number of samples of pine needle oil have been investigated by the authors, partly to provide data for the detection of sophistication, and partly to determine the various constituents; the latter have been identified both by their physical properties and by the preparation of well-characterised derivatives. The rotatory powers were observed in a 100-mm. tube. The oil from the needles of *Abies pectinata*, D.C., is laevorotatory; the sp. gr. = 0.875 at 15°; the rotatory power = $-20^{\circ} 40'$; on distillation under ordinary pressure, 8 per cent. passes over at 150—170°, and 55 per cent. at 170—185°; at higher temperatures, decomposition takes place. The oil consists of laevopinene, laevolimonene, laevobornyllic acetate (4.5 per cent.), and sesquiterpene (Wallach's cadinene).

Pine twig oil from *Abies pectinata*, D.C., has been investigated by Wallach; the sp. gr. = 0.854; rotatory power = -72° ; on distillation, 16 per cent. passes over at 150—170°, and 76 per cent. at 170—185°. The oil consists of laevopinene, laevolimonene, and bornyllic acetate (about 0.5 per cent.).

Spruce oil from *Abies canadensis*, L., consists of laevopinene, laevobornyllic acetate (36 per cent.), and cadinene. The sp. gr. = 0.907°; the rotatory power = $-20^{\circ} 54'$; 11 per cent. passes over at 150—170°, and 37 per cent. at 170—185°.

The needles and twigs of *Picea vulgaris*, Lk., yield an oil of sp. gr. = 0.888 at 15°; the rotatory power = $-21^{\circ} 40'$; 20 per cent. distils at 160—170°, and 50 per cent. at 170—185°; the oil consists of laevopinene, laevophellandrene, dipentene, laevobornyllic acetate (8.3 per cent.), and cadinene.

The oil of *Pinus pumilio*, Haenke, has already been investigated by Atterberg (*Ber.*, 14, 2530); the sp. gr. = 0.865 at 15°; the rotatory power = -9° ; 70 per cent. distils at 170—185°; the oil consists of laevopinene, laevophellandrene, silvestrene, bornyllic acetate (5 per cent.), cadinene, and probably a little dextropinene.

Swedish pine needle oil from *Pinus silvestris*, L., is dextrorotatory, = $+10^{\circ} 40'$; the sp. gr. = 0.872 at 15° ; 44 per cent. distils at 160 — 170° , and 40 per cent. at 170 — 185° ; the oil consists of dextropinene, dextrosilvestrene, and probably bornylic acetate. A sample of oil of the same kind as that just described, but from trees grown in Germany, is also dextrorotatory, = $+10^{\circ}$; the sp. gr. = 0.886 at 15° ; 10 per cent. distils at 160 — 170° , and 46 per cent. at 170 — 185° . The oil is composed of dextropinene, dextrosilvestrene, and cadinene, an acetate which is probably the bornyl salt, and perhaps a little dipentene.

The characteristic odour of pine oils is due to the presence of bornylic acetate. The authors have prepared both modifications synthetically; the lævorotatory compound is identical with the natural product; the dextrorotatory modification only differs in the sign of its rotation. The acetate is deposited from light petroleum in large, hemihedral crystals belonging to the rhombic system; for the dextro-modification $a : b : c = 0.69653 : 1 : 0.45362$; for the natural lævo-modification $a : b : c = 0.69934 : 1 : 0.46171$; it melts at 29° , boils at 98° ; the sp. gr. = 0.091; the rotatory power = $38^{\circ} 20'$. *Bornylic formate* boils at 90° ; the sp. gr. = 1.013; refractive power = $+31^{\circ}$. *Bornylic propionate* boils at 109 — 110° ; sp. gr. = 0.979° ; refractive power = $+24^{\circ}$. *Bornylic butyrate* boils at 120 — 121° ; sp. gr. = 0.966; refractive power = $+22^{\circ}$. *Bornylic valerate* boils at 128 — 130° ; sp. gr. = 0.956° ; refractive power = $+20^{\circ}$. The boiling points of the above salts were observed under a pressure of 10 mm., the sp. gr. at 15° ; they resemble the acetate in general properties, but the characteristic odour decreases with increasing molecular weight.

J. B. T.

Isonitrosocamphor. By G. ODDO (*Gazzetta*, **23**, i, 300—306; compare Abstr., 1889, 619; 1893, i, 422).—The *ethyl* derivative of isonitrosocamphor, $C_{10}H_{14}O:NOEt$, is obtained by digesting a mixture of sodium ethoxide, ethylic iodide, isonitrosocamphor, and alcohol in a reflux apparatus. It forms white, waxy scales melting at 72 — 73° , and is very soluble in alcohol, ether, benzene, or chloroform, but insoluble in water or cold alkalis; it is almost odourless, and is hydrolysed by alcoholic potash with production of isonitrosocamphor. The *methyl* derivative can be obtained by a similar method, but only in an impure state as a yellow oil. On heating isonitrosocamphor with acetic chloride, a *substance*, $C_{12}H_7NO_2$, is obtained, which forms six-sided prisms melting at 172° , and is not a simple acetyl derivative; it is soluble in alcohol, benzene, or chloroform, but only sparingly in ether. When hydrolysed by alcoholic potash, it does not give isonitrosocamphor, but a *substance* which forms prismatic needles melting at 143 — 144° . Benzoic chloride acts readily on isonitrosocamphor at 100° ; the author has, however, not yet succeeded in obtaining the products in a crystalline state.

W. J. P.

The Camphor Group. By U. ALVISI (*Gazzetta*, **23**, i, 332—341; compare Abstr., 1892, 1343).— β -Dibromocamphor readily reacts with phenylhydrazine at 100° , yielding a substance of the composition $C_{10}H_{14}(N_2HPh)_2$, which may be purified by reason of its non-volatility in a current of steam; it is a yellow, amorphous powder melting at

68.5°, and is soluble in alcohol, ether, benzene, or acetic acid, but insoluble in water. When boiled with hydrochloric acid, it undergoes partial resinification, and with acetic chloride it yields an *acetyl* derivative, $C_{10}H_{14}(N_2PhAc)_2$, as an amorphous powder. It also gives resinous products on reduction with sodium amalgam, and does not yield a chlorinated hydrocarbon by Baeyer and Zincke's reaction (Abstr., 1892, 842).

Potassium permanganate, in alkaline or acid solution, oxidises β -dibromocamphor with evolution of carbonic anhydride; a syrupy acid is obtained, but no conclusion as to its composition could be derived from analyses of its insoluble lead and barium salts.

Campholenic acid and phenylhydrazine react in the cold yielding *phenylhydrazine campholenate*, $PhN_2H_2.C_{10}H_{16}O_2$; it forms acicular needles melting at 48.5–49.5°, and on heating at 50–100° loses weight and resinifies. The base and acid react violently when heated together, ammonia being evolved.

W. J. P.

Dextrogyrate Licareol. By P. BARBIER (*Compt. rend.*, 116, 1459–1461).—Essence of coriander, on fractionation, yields a hydrocarbon, $C_{10}H_{16}$, boiling at 165–180° under the ordinary pressure, an oxidised compound which boils at 120° under a pressure of 16 mm., and which will be described subsequently, and an alcohol, *coriandrol*, boiling at 92–93° under a pressure of 15.5 mm. (Abstr., 1882, 525).

Coriandrol is a colourless liquid, with an odour very different from that of licareol, but in other physical properties the two compounds are practically identical, except that coriandrol is dextrogyrate.

	Coriandrol.	Licareol.
Boiling point.....	196–198°	198–200°
Sp. gr. at 0°.....	0.8820	0.8819
Refractive index.....	$\left\{ \begin{array}{l} n_r \\ n_b \end{array} \right.$	$\left\{ \begin{array}{l} 1.4641 \\ 1.4781 \end{array} \right.$
Rotatory power.....	+15° 1'	–18° 21'

Coriandrol, like licareol, yields a liquid tetrabromide, and when carefully oxidised, it yields an aldehyde, $C_{10}H_{16}O$, practically identical with licaraldehyde in physical properties. When subjected to the action of strong oxidising agents, coriandrol yields the same products as licareol; the author was unable to confirm Grosser's statement that it yields dimethylsuccinic acid (*loc. cit.*). With hydrogen chloride, it yields a liquid dihydrochloride identical with that obtained from licareol, and when treated with acetic anhydride it yields a limonene which cannot be distinguished from licarene, and at the same time there is formed the acetate of an alcohol which appears to be identical with licarhodol.

It would seem from these results that coriandrol must be regarded as dextrogyrate licareol.

C. H. B.

Constitution of Rhodinol. By P. BARBIER (*Compt. rend.*, 117, 177–178).—*Rhodinol*, $C_{10}H_{18}O$, a constituent of the liquid portion of

oil of roses, has been shown by Eckart (Abstr., 1892, 203, 625) to be a primary alcohol, yielding valeric acid as one of the products of oxidation, and having a formula containing two ethylene bonds. It is thus an isomeride of licareol (compare this vol., i, 496) and geraniol. Rhodinol is an oily liquid, boiling at $126\cdot5^{\circ}$ under a pressure of 16 mm., and having a sp. gr. of $0\cdot8956$ at 0° , refractive indices $n = 1\cdot4653$ for $\lambda 645$ and $n = 1\cdot4795$ for $\lambda 452\cdot6$, and a specific rotatory power $[\alpha]_D = -2^{\circ} 37'$ at 25° . When treated with gaseous hydrogen chloride, it yields dipentene dihydrochloride, which boils at 147° under a pressure of 18 mm., has a sp. gr. of $1\cdot051$ at 0° , and is converted by a boiling acetic acid solution of potassium acetate into dipentene, recognised by its characteristic bromide melting at 124° . The formula deduced from these various reactions is $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHPr}\cdot\text{CH}_2\cdot\text{OH}$. To determine which of the two possible stereometric formulæ is to be assigned to rhodinol, the latter was heated with acetic anhydride at 180° . The *acetate* thus formed is a colourless, mobile liquid of agreeable odour, boiling at 131° under a pressure of 15 mm., and having a sp. gr. of $0\cdot9214$ at 0° , and refractive indices $n = 1\cdot4526$ for $\lambda 645$ and $n = 1\cdot4661$ for $\lambda 452\cdot6$. When hydrolysed with alcoholic potash, it is reconverted into an alcohol, identical with rhodinol, which is therefore the stable modification.

JN. W.

Bulgarian (Turkish) Oil of Roses. By V. MARKOVNIKOFF and A. REFORMATSKY (*J. Russ. Chem. Soc.*, **24**, 663—686).—The material examined by the authors consisted of three rose oils from different parts of Bulgaria, which liquefied completely at $23\cdot5^{\circ}$, 24° , and 24° respectively, and had the sp. gr. $0\cdot8563$, $0\cdot8603$, and $0\cdot8639$ at $27\cdot5^{\circ}/0^{\circ}$. At the ordinary temperature, they were thick, yellowish liquids, containing transparent, crystalline plates, and having a strong odour of roses, modified by a slightly fasty smell. They were all optically active, rotating the plane of polarisation about $3\cdot5^{\circ}$ to the left in a 100 mm. tube.

In order to effect a separation of the elæoptene and stearoptene contained in it, the oil was cooled to 0° and filtered, the filtrate being cooled to -55° , and refiltered until no more solid separated. The liquid elæoptene obtained in this way, when dried over fused potash, was a yellowish, mobile liquid, the rotation of which in a 100 mm. tube was $-3^{\circ} 44'$. On repeated distillation at the ordinary pressure, it yielded as chief fraction a liquid boiling at $222-222\cdot5^{\circ}$ ($224\cdot7^{\circ}$, corr.), and when freshly distilled had the composition represented by the formula $\text{C}_{10}\text{H}_{20}\text{O}$. This substance was shown to be an alcohol, and the authors have named it *roseol* (roseolic alcohol). Roseol smells of oil of geraniums, but on standing in the air it rapidly oxidises, thereby acquiring the odour of roses. It is a colourless, fairly mobile liquid, with a sp. gr. = $0\cdot87846$ at $20^{\circ}/20^{\circ}$ and $0\cdot87498$ at $20^{\circ}/4^{\circ}$. Its molecular refractive power at 20° , according to Lorentz's formula, is $R_a = 49\cdot48$.

Its solution in carbon tetrachloride at once decolorises a solution of bromine in the same solvent, the amount of bromine disappearing being 3 atoms per molecule of roseol. A separate experiment showed

that 2 atoms of bromine are absorbed without evolution of hydrogen bromide.

The acetate, $C_{10}H_{19}OAc$, formed by heating 9 parts of roseol with 7 of acetic anhydride for 24 hours on a sand bath, boils at $235-236^{\circ}$, and is a colourless, pleasant-smelling liquid.

On oxidation at the ordinary temperature with 1 per cent. potassium permanganate solution, roseol yields no products volatile with steam, but gives a syrup which distils at 240° under 100 mm. pressure. Analysis showed this to be the *glycerol* $C_{10}H_{19}(OH)_3$, a thick, faintly yellow liquid, which does not solidify at -50° . It has a faint odour of roses, and a taste at first sweet, but afterwards burning. Its sp. gr. at $0^{\circ}/0^{\circ}$ is 1.0445, and at $20^{\circ}/0^{\circ}$ 1.0343. It is easily soluble in water, but only slightly in alcohol or ether. Bromine is not decolorised by it, even on long standing. The *triacetate*, $C_{10}H_9(OAc)_3$, formed by heating the glycerol at 150° with excess of acetic anhydride, boils at $215-220^{\circ}$ under 40 mm. pressure, and solidifies at -10° . It has an aromatic odour, and a sp. gr. = 1.0594 at $0^{\circ}/0^{\circ}$.

Roseol (5 grams) was dissolved in 10 times its volume of light petroleum, and added drop by drop to phosphoric anhydride (2 grams), covered by the same solvent, and cooled in ice. After remaining for two hours at the ordinary temperature, the light petroleum was poured off, washed with sodium carbonate solution, dried, and distilled on the water bath. The residue, on fractionation, yielded as chief product a liquid boiling at $180-185^{\circ}$, and having the composition $C_{10}H_{18}$. This hydrocarbon is a very mobile and slightly fluorescent liquid, which smells of camphor, and oxidises rapidly in the air. No terpene could be detected in the crude hydrocarbon.

When heated for 12 hours at $180-200^{\circ}$ with 40 volumes of hydriodic acid saturated at 0° , roseol gives a saturated hydrocarbon $C_{10}H_{22}$, which boils at $158-159^{\circ}$, has the vapour density 4.91, and sp. gr. = 0.7554 at $20^{\circ}/0^{\circ}$.

The authors contend that their results prove the chief constituent of the elæoptene of rose oil to be an unsaturated alcohol of the formula $C_{10}H_{20}O$, isomeric with allyldipropylcarbinol (b. p. 192°) and allyldiisopropylcarbinol (b. p. $169-171^{\circ}$). Judging from the high boiling point (220°), it is probably normal. The results obtained by Eckart (Abstr., 1891, 323; 1892, 203, 625), who stated that the chief constituent of Turkish rose oil elæoptene was rhodinol, $C_{16}H_{18}O$, are questioned on the ground that he worked with impure (partially oxidised) material (compare, however, preceding abstract).

The solid *stearoptene* obtained from the original oil by freezing constituted about 20 per cent. of the whole. It was recrystallised several times from 98 per cent. alcohol, in which it is moderately soluble, and dried first over sulphuric acid, afterwards for a short time at 100° . The purified substance melted at $36.5-36.8^{\circ}$, solidified at 34° , and boiled between 350° and 380° ; analysis and a molecular weight determination in benzene showed that it is a saturated hydrocarbon of the formula $C_{16}H_{34}$. Small quantities of other hydrocarbons were also found to be present.

J. W.

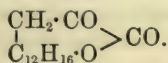
Geraniol. By P. BARBIER (*Compt. rend.*, **117**, 120—122).—Essence of *Andropogon schœnanthus*, when fractionated, yields about 75 per cent. of geraniol, mixed with a small quantity of a sesquiterpene, which increases its specific gravity and renders it lœvorotatory. When this geraniol is heated with acetic anhydride in a sealed tube at 150°, it yields only the acetate $C_{10}H_{17}OAc$, a colourless, mobile liquid, which has a pleasant odour, and boils at 129—130° under a pressure of 14.5 mm.; sp. gr. at 0° = 0.9388; refractive index at 24°, $n = 1.4614$ for $\lambda 645$ and $n = 1.4758$ for $\lambda 452.6$. When heated with alcoholic potash, this acetate rapidly hydrolyses, and yields pure geraniol, a colourless, slightly oily liquid, with a fine odour; it boils at 126—127° under a pressure of 16 mm.; sp. gr. at 0° = 0.9012; refractive indices at 24°, $n = 1.4750$ for $\lambda 645$ and $n = 1.4904$ for $\lambda 452.6$. With hydrogen chloride, it yields a liquid dihydrochloride, boiling at 142—143° under a pressure of 16 mm., and when this is treated with a boiling solution of potassium acetate in acetic acid, it yields dipentene.

The author considers that the product obtained by Bouchardat by the action of acetic anhydride on linalol (this vol., i, 544) is lica-rhodol and not geraniol, the linalol itself being the unstable stereo-isomeride of geraniol.

C. H. B.

Santonin. By J. KLEIN (*Arch. Pharm.*, **231**, 213—234; compare this vol., i, 111 and 363).—The author confirms his previous observation of the production of α -santigendilactone by the reduction of santonin with zinc in acetic acid solution; santonone, $(C_{15}H_{17}O_2)_2$, contrary to the statement of Grassi-Cristaldi (this vol., i, 110), does not appear to be formed. The action of phosphoric chloride on santonin has already been described (this vol., i, 425). Santonin oxime crystallises with $1H_2O$. The acetyl derivative, $C_{15}H_{18}NO_3Ac$, melts at 165—166° or at 169—170° with decomposition, according to the rapidity with which it is heated, instead of at 201—203° as stated by Gucci, and is readily hydrolysed by alcoholic potash or ammonia. The benzyl derivative, $C_{15}H_{18}NO_3 \cdot C_7H_7$, crystallises in needles melting at 151—152°. The oxime may also be prepared in alkaline solution; on acidification with hydrochloric acid, it gives a violet-red coloration with ferric chloride, which probably points to the existence of a syn-hydroximic acid. On dissolving the oxime in alkali, and subsequently acidifying and adding ferric chloride, a yellow colour is produced, indicating the existence of an "anti-" acid; the "syn-" compound is tolerably stable in solution, but cannot be reconverted into its isomeride.

The paper concludes with a discussion of the constitution of santonin, and a criticism of the work of several Italian chemists on the subject. The author is of opinion that the properties and reactions of santonin can only be explained on the assumption that it is the α -lactone of a hydroxy- α -ketonic acid of the formula



J. B. T.

Oxidation Products of the Santononic acids. Diparaxylyl and Diphenyl. By G. GRASSI-CRISTALDI (*Gazzetta*, 23, i, 306—308).—The author hopes to demonstrate the production of diphenyl and diparaxylyl during the oxidation of the isomeric santononic acids with nitric acid; he has, however, not yet analysed the products of the reaction.

W. J. P.

Derivatives of Photosantononic acid. By S. CANNIZZARO and P. GUCCI (*Gazzetta*, 23, i, 286—294).—On passing a current of dry hydrogen chloride through a solution of photosantononic acid in 90 per cent. alcohol, and distilling off the solvent under reduced pressure, a mixture of dextro- and inactive dehydrophotosantononic acids is obtained; the quantity of the active acid produced decreases as the time of passing hydrogen chloride through the solution increases, and if the solution is boiled during treatment with the gas, only the inactive acid is obtained (compare Abstr., 1886, 73; 1892, 869).

On heating either the active or inactive acid considerably above its melting point, or on distilling it under reduced pressure at 290—300°, a new bibasic isomeride seems to be produced; it forms very hard prisms melting at 133·5—134·5°, and is inactive. All the three acids, when distilled with barium oxide, yield a hydrocarbon, $C_{13}H_{20}$. On oxidation with chromic acid mixture, this substance and the three isomeric dihydrophotosantononic acids all give a dimethyl-phthalidecarboxylic acid, $\begin{array}{c} HC \cdot CH : C \cdot CMe_2 \\ | \qquad | \\ COOH \cdot C \cdot CH : C \cdot CO \end{array} > O$, which crystallises in long, white needles melting at 205—206°; its ethylic salt forms white prisms which melt at 105—106°. On heating in a sealed tube at 180—190° with hydriodic acid, the acid yields a white substance melting at 236—236·5°; this may be reconverted into the acid by oxidising agents. When distilled with baryta at 350°, the acid gives benzene, and, on heating with potash, it yields isophthalic acid.

W. J. P.

Preparation of Pure Digitonin. By H. KILIANI (*Arch. Pharm.*, 231, 460—461).—The solution in hot 85 per cent. alcohol of the crude substance ("digitalinum pur. pulv.," compare Abstr., 1891, 576) should not be allowed to cool, but should be placed on a water bath at 45°, kept for six hours at this temperature, and then allowed to cool slowly. The glucoside is then deposited in a form in which it is much more easily drained by the pump.

C. F. B.

Derivatives of Digitogenin. By H. KILIANI (*Arch. Pharm.*, 231, 448—460).—The action of various reagents on digitic acid was tried, but no well-characterised products could be obtained. The mother liquors from digitic acid, prepared by oxidising digitogenic acid with alkaline permanganate (Abstr., 1891, 576), when oxidised with alkaline permanganate on the water bath, yield a bibasic acid which forms hard granules or minute needles which soften at 170°. It forms a potassium salt, $C_9H_{13}O_4K + C_9H_{14}O_4 + 7H_2O$, crystallising in minute needles, and is possibly identical with the isocamphopyric acid prepared by Marsh, Balliol, and Gardner by distilling camphoic acid

(Trans., 1891, 651). By reducing digitogenic acid with sodium amalgam, *d-oxydigitogenic acid*, $C_{14}H_{22}O_3 + \frac{1}{2}H_2O$, is obtained; it forms minute, nacreous plates, and begins to soften at about 240° . When digitogenic acid is boiled with potash and dilute alcohol, carbonic anhydride is eliminated, and two acids are formed; of these, *hydrodigitoic acid*, $C_{13}H_{22}O_3$, occurs in far smaller quantity; it softens at 240° , crystallises from 93 per cent. alcohol in silky needles, and yields a *magnesium salt*, $(C_{13}H_{21}O_3)_2Mg + 5H_2O$, forming white, nodular aggregates. By the cautious addition of water to the alcoholic mother liquor, and allowing the mixture to remain for a time, colourless prisms of *digitoic acid*, $C_{13}H_{20}O_3 + \frac{1}{2}H_2O$, are deposited; this acid melts at 210° , yields a *magnesium salt*, $(C_{13}H_{19}O_3)_2Mg + 8H_2O$, crystallising in nodular aggregates with a greasy lustre, and is converted by further oxidation into digitic acid.

C. F. B.

Crystalline Substance from Santalum Praesii. By A. BERKENHEIM (*J. Russ. Chem. Soc.*, **24**, 688—690).—The author has investigated a crystalline substance obtained by Schimmel and Co. from *Santalum Praesii*. On recrystallisation, it forms large prisms melting at 101 — 103° , and having the composition represented by the formula $C_{15}H_{24}O_2$. On heating with acetic anhydride, it gives an acetate, $C_{15}H_{23}O_2Ac$, which crystallises in large, hexagonal plates, and melts at 68.5 — 69.5° . Phosphorus pentachloride has no action on the acetate, but phosphorus trichloride, with the original substance, gives a chloro-derivative, $C_{15}H_{23}OCl$, which melts at 119 — 120.5° . The original substance gives a sodium derivative from which the methyl ether is obtained in the liquid state. Oxidation with potassium permanganate yields an acid $C_7H_{14}O_2$.

J. W.

Gum Benzoin from Siam. By F. LÜDY (*Arch. Pharm.*, **231**, 461—480; compare this vol., i, 480).—Gum benzoin (from Siam) is soluble in ether, and the dissolved substance yields no ash when ignited. It contains (1) vanillin, 0.15 per cent.; (2) free benzoic acid; (3) 0.3 per cent. of an oily, neutral substance which is an ethereal salt of benzoic acid; (4) a mixture of a little *benzoresinylic benzoate* with much *siaresinotannyllic benzoate*, this mixture forming the main constituent of the gum. In addition to these, woody impurities are present to the extent of 1.6—3.3 per cent. No cinnamic acid, either free or combined, could be detected. By hydrolysis of the mixture of benzoresinylic and siaresinotannyllic benzoates, benzoic acid and a mixture of benzoresinol and siaresinotannol are obtained in the proportion of about 1 : 11. The benzoresinol is identical with the substance obtained from Sumatra benzoin; it crystallises from acetone in groups of long, white prisms, and melts at 272° (uncorr.). *Siaresinotannol*, $C_{12}H_{14}O_3$, is a brown powder, resembling in its properties the resinotannol obtained from Sumatra benzoin. It yields a *potassium derivative*, $C_{12}H_{13}O_3K + H_2O$, crystallising in yellow needles, and an *acetyl derivative*, $C_{12}H_{13}AcO_3$, as a yellow, amorphous powder. Nitric acid has the same action on it as on Sumatra resinotannol.

C. F. B.

A Ketone obtained from Ethylic Dihydrocollidinedicarboxylate. By F. GARELLI (*Gazzetta*, 23, i, 569—579).—Amongst the products obtained by Hantzsch (Abstr., 1886, 77) on heating ethylic dihydrocollidinedicarboxylate with dilute hydrochloric acid in a closed tube at 120°, is a ketone of the composition $C_8H_{12}O$.

When this ketone is heated with alkali and benzaldehyde, it yields a condensation product of the composition $C_{15}H_{16}O$; this crystallises in beautiful rosettes melting at 99°. It gives a crystalline *oxime* which melts at 133—134°, and is soluble in alcohol, ether, benzene, and acetic acid; no acetyl derivative could be prepared from it. The *hydrazone*, $C_{15}H_{16}:N_2HPh$, is obtained in small, yellow needles melting at 180°. The condensation product is readily oxidised by dilute alkaline permanganate, yielding benzoic and acetic acids.

W. J. P.

Cryoscopic Behaviour of some Acetates of Feeble Bases. By A. GHIRA (*Gazzetta*, 23, i, 341—346; compare Kononoff, this vol., ii, 357, and Nasini and Pezzolato, *ibid.*, i, 444).—The author has determined the molecular depressions of the freezing points of water and benzene by the acetates of aniline, pyridine, diethylaniline, nicotine, quinoline, diisoamylamine, diisobutylamine, propylamine, and allylamine, and by acetanilide. In aqueous solution, all these substances behave as if completely dissociated; the benzene solutions, however, show considerable diversity of behaviour. Nicotine acetate in dilute benzene solutions gives almost normal molecular depressions, whilst aniline acetate, under similar circumstances, seems to behave as a mixture of the base with acetic acid.

W. J. P.

Derivatives of Quinoline. By A. CLAUS (*J. pr. Chem.* [2], 48, 135—140).—In reviewing the present state of our knowledge as to the orientation of quinoline substitution products, the author points out that the nitro- and sulphonic radicles invariably enter the benzene ring, whereas bromine will always take the 4' position if this be unoccupied; chlorine, on the other hand, does not show this affinity for the 4'-position. With regard to the influence of already existing substituting groups on the orientation of entering groups, it is noted that the existence of bromine in the benzene ring does not influence the entry of a new bromine atom into the 4'-position. The case is somewhat different when hydroxy-groups occur in the benzene ring. Thus it has been shown (Abstr., 1892, 353) that the first bromine atom which enters into 1- and 3-hydroxyquinoline gives rise to a 4-bromo-derivative; the same holds good for the entry of a chlorine atom into these hydroxyquinolines, nor will the second bromine or chlorine atom take the 4'-position. A third bromine atom can be introduced into 1-hydroxyquinoline by treatment of 1:4-hydroxyquinolinesulphonic acid with phosphorus bromide, and this atom takes the 4'-position; but in this respect chlorine and bromine differ, for no trichloro-1-hydroxyquinoline, containing a 4'-chlorine atom, has yet been prepared.

The entry of bromine into a quinoline-1-sulphonic acid may take place either in the 3- or 4'-position, according to the experimental conditions.

A. G. B.

1-Chloroquinoline. By A. CLAUS and M. SCHÖLLER (*J. pr. Chem.* [2], 48, 140—151).—1-Chloroquinoline, prepared from orthochloraniline by Skraup's method, is a nearly colourless oil, which quickly becomes brown on exposure to light and air; it boils at 288° , and is not solid at -20° ; it is freely soluble in most organic solvents, and markedly soluble in water. If crude chloraniline, containing both the ortho- and the para-compounds, be employed for making 1-chloroquinoline, the latter can afterwards be separated from the 3-chloroquinoline by dissolving the mixture in alcohol and adding nitric acid, when the 3-derivative is precipitated as nitrate. 1-Chloroquinoline hydrochloride crystallises in colourless needles, melts in its water of crystallisation at $96-97^{\circ}$, and dissolves freely in alcohol and in water. The *platinochloride*, $(C_9NH_6Cl)_2 \cdot H_2PtCl_6 + 2H_2O$, forms small, yellow needles, and melts, when anhydrous, at 235° with decomposition. The *nitrate* melts in its water of crystallisation at $86-87^{\circ}$, and dissolves freely in water, but less freely in alcohol. The *dichromate*, $(C_9NH_6Cl)_2 \cdot H_2Cr_2O_7$, crystallises in lustrous, orange laminæ, melts, with carbonisation, at $160-161^{\circ}$, and dissolves freely in hot water. The *methiodide*, $C_9NH_6Cl \cdot MeI$, crystallises in hard, yellow needles and short prisms, darkens and melts at 165° , and dissolves in hot water and alcohol, but not in ether. The *methochloride* crystallises in colourless laminæ and flat prisms, melts at 140° , and dissolves in water; its *platinochloride*, $(C_9NH_6Cl \cdot MeCl)_2 \cdot PtCl_4$, melts, with decomposition, at 248° .

4: 1-Nitrochloroquinoline is the sole product of the nitration of 1-chloroquinoline; it crystallises in thin, colourless needles, melts at 144° , and dissolves in hot alcohol and in ether. The *platinochloride* is anhydrous, and melts with decomposition at 260° .

4: 1-Amidochloroquinoline, obtained in the usual way, crystallises in lustrous, colourless aggregates of needles, which soon become yellow or red; it melts at 152° , and is not volatile with steam; organic solvents dissolve it freely. The *hydrochloride* crystallises in brilliant, thick, red, anhydrous prisms, and melts at 275° ; the *platinochloride*, with $2H_2O$, is described. 1: 4-Chloroquinoline diazochloride forms red needles; by treatment with cuprous chloride, it yields 1: 4-dichloroquinoline, melting at 94° , identical with that prepared by La Coste (*Abstr.*, 1882, 979); its *platinochloride* melts at 252° with decomposition.

1: 4-Chloroquinolinesulphonic acid crystallises with $2H_2O$ in brilliant, colourless, transparent, lustrous prisms or needles, and in rhombic tables; it has no definite melting point. The *ammonium* salt is described, as are also the *sodium* salt, with $5H_2O$; the *barium* salt, with $7H_2O$; the *silver* salt; the *copper* salt, with $4H_2O$; and the *ethylic* salt, melting at 140° .

A. G. B.

1-Bromoquinoline. By A. CLAUS and H. HOWITZ (*J. pr. Chem.* [2], 48, 151—160).—1-Bromoquinoline (*Abstr.*, 1888, 163) is a colourless, or pale yellow, oil; it boils at $302-304^{\circ}$, and is not solid at -10° . The *platinochloride* crystallises with $2H_2O$ and also with $3H_2O$, and melts with decomposition at 252° . The *methiodide*, $C_9NH_6Br \cdot MeI$, forms long, yellow, anhydrous needles and prisms, and

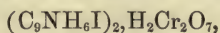
melts at 280—281°. The *ethiodide* crystallises in yellowish-green needles or thick, yellow, prismatic aggregates, and melts at 183° with gradual decomposition.

4:1-*Nitrobromoquinoline* crystallises in colourless needles, melts at 137—138°, and sublimes unchanged; its *platinochloride* is described. 4:1-*Amidobromoquinoline* forms yellow needles or thick prisms, melts at 128—130°, and sublimes; it dissolves in acids with an intensely red coloration, and is precipitated from these solutions by ammonia; its *platinochloride* is described. 4:1-*Dibromoquinoline* was obtained from the amido-derivative through the diazo-reaction; it crystallises in long, colourless needles, and melts at 127°. A compound melting at 162°, whose nature has yet to be elucidated, was formed at the same time.

1:4'-*Amidobromoquinoline*, prepared from the nitro-4'-bromoquinoline (m. p. 124°) which is always formed as a bye-product in the preparation of 4:4'-nitrobromoquinoline, crystallises in long, straw-coloured needles, melts at 107—108°, and dissolves in alcohol. The *hydrochloride* melts with decomposition at 252°; the *platinochloride* is described. As the amido-derivative yields 1:4'-dibromoquinoline (Abstr., 1890, 1320) through the diazo-reaction, the orientation of the parent nitro-derivative is settled as 1:4'-nitrobromoquinoline.

A. G. B.

Iodoquinolines. By A. CLAUS and P. GRAU (*J. pr. Chem.* [2], 48, 160—169).—1-*Iodoquinoline* is prepared by diazotising 1-amidoquinoline and treating the diazo-compound with potassium iodide and copper; it crystallises in colourless, vitreous needles, which become brown when exposed to light and air; it melts at 136° and dissolves in hot water and in most organic solvents. The *hydrochloride*, $C_9NH_6I \cdot HCl$, crystallises in short, thick, yellow prisms, and melts at 183°; the *platinochloride* is described. Halogen alkyl compounds and nitro-derivatives have not been obtained. The *dichromate*,



melts with decomposition at 135°; the *nitrate*, also with decomposition, at 154°.

3-*Iodoquinoline*, prepared from 3-amidoquinoline, crystallises in nacreous, nearly colourless laminæ, and sublimes in the form of needles; it melts at 88° and dissolves in hot water and in most organic solvents. The *dichromate*, the *hydrochloride*, melting at 210°, and the *platinochloride*, melting with decomposition at 265°, are described. The *methiodide* crystallises in brilliant, yellow, transparent, vitreous prisms and long needles, and is unchanged at 300°.

4-*Iodoquinoline*, from 4-amidoquinoline, crystallises in small, colourless, vitreous needles and sublimes in the same form; it melts at 100° and dissolves very slightly in hot water, but freely in most organic solvents. The *dichromate* melts with decomposition at 165°; the *hydrochloride* becomes dark and melts at 235°; the *platinochloride* melts with decomposition at 263°; the *methiodide* crystallises in fern-like aggregates of small, yellow needles, and melts with decomposition at 245°.

2-*Iodoquinoline*, from 2-amidoquinoline (see next abstract), forms

small, colourless needles, melts at 103° , and resembles the foregoing iodoquinolines in properties. A. G. B.

2-Nitroquinoline and its Derivatives. By A. CLAUS and C. MASSAU (*J. pr. Chem.* [2], **48**, 170—179).—2-Nitroquinoline has been already described (Abstr., 1888, 295); it crystallises in plates or needles, and melts at 132 — 134° . The *methiodide* forms brilliant, dark red, transparent crystals of various ill-defined forms, and melts at 231 — 233° with decomposition. The *methochloride* melts with decomposition at 212 — 213° . The *methonitrate*, obtained by acting on the methiodide with silver nitrate, crystallises in prisms and melts with decomposition at 170° . The *ethiodide* melts with decomposition at 220° .

2-Amidoquinoline crystallises in yellowish-white needles, which are unstable in air; it is very slightly volatile with steam, melts at 188 — 190° , and sublimes. The *platinochloride* melts with decomposition at 225° . The conversion of 2-amidoquinoline into 2-hydroxyquinoline may be effected through the diazo-reaction, but better by heating with hydrochloric acid at 220° ; the preparation of the corresponding bromo-, chloro-, and iodo-derivatives from the amidoquinoline may also be effected through the diazo-reaction.

A. G. B.

Hydroxy-derivatives of Anthraquinolinequinone. By C. GRAEBE and A. PHILIPS (*Annalen*, **276**, 21—35).—Bohn obtained certain blue and green dyes by heating dihydroxyanthraquinolinequinone ("alizarin-blue") with ordinary or fuming sulphuric acid (Badische Anilin- und Soda-Fabrik, German Patents of 1888, Nos. 46654 and 47252). These dyes have been shown by Graebe (Abstr., 1891, 463) to contain higher hydroxy-derivatives (compare also Schmidt and Gattermann, Abstr., 1891, 1382); subsequently, the method was extended by Bohn and by Schmidt and Gattermann (Abstr., 1891, 935) to the preparation of polyhydroxy-derivatives of anthraquinone from alizarin.

The authors find that the derivatives of anthraquinolinequinone, like the corresponding ones of anthraquinone, are the "darker" in colour the more hydroxyl groups they contain (compare below).

Hydroxyanthraquinolinequinone, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{C}_6\text{H}(\text{OH}) < \begin{smallmatrix} \text{CH}:\text{CH} \\ \text{N}=\text{CH} \end{smallmatrix}$ [OH = 3' or 4'], is prepared as follows:—"Alizarin-blue" is converted into amidohydroxyanthraquinolinequinone by heating it at 160° with aqueous ammonia of 0.95 sp. gr.; the amido-derivative is then dissolved in concentrated sulphuric acid mixed with one-fourth its volume of water, treated at 0° with sodium nitrite, and the liquid poured into boiling alcohol and boiled for a quarter of an hour; the hydroxyanthraquinolinequinone is precipitated by the addition of water. It crystallises in brick-red prisms, melts at 208° , and is as good as insoluble in water, sparingly soluble in ether, but more readily in alcohol. It dissolves in concentrated sulphuric acid with a yellowish-brown coloration, the sulphate being precipitated on diluting with water; in ammonia, it dissolves with a cherry-red coloration.

tion, and in alkalis with a violet coloration; in presence of an excess of alkali, and especially on boiling, the violet alkali salts separate. The *benzoyl* derivative, $C_{17}NH_5O_2 \cdot OBz$, forms brown crystals, and melts at 175° .

Trihydroxyanthraquinolinequinone $[(OH)_3 = 3' : 4' : 4 \text{ or } 3' : 4' : 1]$ ("hydroxylizarin-blue") may be obtained from the portion of crude "alizarin-green" (not the bisulphite compound) which is insoluble in nitrobenzene, by heating it at 180° with hydrochloric acid or by sublimation; it is, however, best prepared by Schmidt and Gattermann's method (Abstr., 1891, 1383). The absorption spectrum of the solution in alcoholic ammonia is almost the same as that of "alizarin-blue," and its solution in concentrated sulphuric acid exhibits an absorption band at 40—45, and a lighter one at 50—56 (Bunsen-Kirchhoff scale). It differs from "alizarin-blue" in being insoluble in aqueous ammonia.

Tetrahydroxyanthraquinolinequinone $[(OH)_4 = 3' : 4' : 4 : 1]$ ("dihydroxylizarin-blue") occurs in small quantity in technical "alizarin-green" and in "alizarin-indigo-blue." When "alizarin-green" is extracted with boiling nitrobenzene, the tetrahydroxy-derivative separates from the filtrate in dark blue crystals; it is also obtained as a sublimate when "alizarin-indigo-blue" is heated. It is insoluble in aqueous ammonia, and is identical with the compound prepared by Schmidt and Gattermann (*loc. cit.*). Its solution in concentrated sulphuric acid exhibits a bright, broad band in the red region at 34—40, and a narrower one in the yellow at 47—51.

Pentahydroxyanthraquinolinequinone $[(OH)_5 = 3' : 4' : 4 : 2 : 1 \text{ or } 3' : 4' : 4 : 3 : 1 ?]$ represents the portion of "alizarin-indigo-blue" soluble in nitrobenzene; it forms a blue, crystalline mass, and is soluble in both aqueous and alcoholic ammonia, as well as in alkalis, forming blue solutions. Its solution in alcoholic ammonia exhibits two faint absorption bands, a narrow one at 37—38 and a broad one at 42.5—48. The absorption spectrum of the solution in concentrated sulphuric acid resembles that of the tetrahydroxy-derivative, but the bands are less distinct, especially that in the yellow region. The *pentabenzoyl derivative* is a reddish-brown, flocculent substance; it melts at 175° , and yields the pentahydroxy-compound when boiled with aqueous alkalis.

As stated by Schmidt and Gattermann, "alizarin-blue-green" contains the sulphonic acid of a trihydroxyanthraquinolinequinone, and "alizarin-green" contains an isomeric acid; the authors have also detected varying amounts of tetrahydroxyanthraquinolinequinone in the last-mentioned dye. "Alizarin-indigo-blue" consists of a mixture of tetra- and penta-hydroxyquinolinequinones.

The authors show that the above-described colouring matters derived from "alizarin-blue" yield quinolinic acid on oxidation with nitric acid, which fact proves that the hydroxyl group and also the sulphonic group in these dyes always enters the benzene nucleus, and not the pyridine nucleus.

A. R. L.

Pyrazole Compounds. By O. SEVERINI (*Gazzetta*, 23, i, 284—286).—The action of sodium hypochlorite on pyrrolidine has been

already investigated by Ciamician and Silber (*Gazzetta*, **16**, 19). On boiling 1-phenylpyrazole with sodium hypochlorite solution, 1-phenylchloropyrazole, $C_6H_7N_2Cl$, is obtained; it is very volatile, and forms beautiful white needles melting at $75-75.5^\circ$. It is insoluble in water, but soluble in alcohol or ether. The chlorine probably occupies the position 4 of the pyrazole nucleus, for sodium hypochlorite does not act on 1-phenyl-4-bromopyrazole.

W. J. P.

Phenylethyldimethylpyrazole. By L. BALBIANO (*Gazzetta*, **23**, i, 323—332; compare Abstr., 1892, 885).—1-Phenylethyldimethylpyrazole, $C_3N_2PhEtMe_2$, is obtained by the action of phenylhydrazine on β -acetylpropionylethane in ethereal solution; it is a yellow oil with an aromatic odour, and boils at 150° under 75 mm. pressure. It is soluble in alcohol or ether, but insoluble in water, and gives the pyrazoline reaction on boiling with soda, and subsequently acidifying and treating with potassium chromate, ferric chloride, or sodium nitrite solution. The *platinochloride*, $(C_3N_2PhEtMe_2)_2H_2PtCl_6 + 2H_2O$, forms beautiful reddish-yellow laminæ, and melts at 175° with decomposition. On heating at about 230° , it absorbs oxygen and yields trioxymethylene and a bright-yellow powder of the composition $(C_3N_2PhEtMe)_2PtCl_2$. The latter substance, on warming with nitrohydrochloric acid, yields *dichloroplatomethylethylphenyltrichloropyrazole*, $(C_{12}H_{10}N_2Cl_3)_2PtCl_2$, as a crystalline powder which is insoluble in water or alcohol.

The author concludes that the platinochlorides of tetra-substituted derivatives of pyrazole undergo the same change on heating as do those of tri-substituted derivatives.

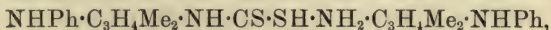
W. J. P.

Synthesis of Homologues of 1-Phenylpyrazole. By L. BALBIANO and G. MARCHETTI (*Gazzetta*, **23**, i, 485—492).—1-Phenylpyrazole *methiodide*, $CH \begin{smallmatrix} \text{CH} \cdot NPh \\ \text{CH} : N, MeI \end{smallmatrix}$, is obtained, in almost quantitative yield, by heating the pyrazole with methylic iodide in a closed tube at 100° ; it forms beautiful, lustrous needles which melt at $178-179^\circ$ with decomposition, is soluble in water or alcohol, and insoluble in ether. When heated in a closed tube at $240-300^\circ$, it yields a mixture of phenylpyrazole and 1-phenyl-4-methylpyrazole, $C_3N_2H_2MePh$, a yellowish oil which has an aromatic odour, boils at $264-265^\circ$, and does not solidify at -15° ; it is insoluble in water. The *platinochloride*, $(C_3N_2H_2MePh)_2H_2PtCl_6 \cdot 2H_2O$, separates from water in yellowish-red needles which melt at $159-160^\circ$ with decomposition; it loses its water in a vacuum over sulphuric acid. When the anhydrous salt is heated at $130-160^\circ$, it gives *dichloroplato-1-phenyl-4-methylpyrazole*, $(C_3N_2H_2MePh)_2PtCl_2$, as a bright-yellow powder which is insoluble in water, and does not melt at 250° . 1-Phenyl-4-methylpyrazole *methiodide*, $C_3N_2H_2MePh, MeI$, is obtained by heating the pyrazole with methylic iodide at 100° in a sealed tube. It is soluble in alcohol and water and separates from the latter solvent in needles which melt at 160° ; the corresponding ethiodide could not be prepared. On oxidation with alkaline permanganate, the pyrazole yields 1-phenylpyrazole-4-carboxylic acid.

W. J. P.

Reduction of Substituted 1-Phenylpyrazoles. By G. MARCHETTI (*Gazzetta*, **23**, i, 425—430).—On reducing an alcoholic solution of 1-phenylpyrazole with sodium by the process previously given by the author (this vol., i, 177) no benzene is obtained and no reduction products could be isolated.

1-Phenyl-3:4-dimethylpyrazole, however, behaves like its 1:3:5-isomeride on reduction (this vol., i, 178), and the product of the reaction by similar treatment yields benzene, 3:4-dimethylpyrazole, and 1-phenyl-3:4-dimethyltetrahydropyrazole; the latter was obtained in very small quantity, and its properties could not be determined. It is energetically oxidised by cold permanganate just as its isomeride is. During the reduction, *dimethylphenyltrimethylenediamine* is also formed; the reduction hence proceeds partly as in the case of 1-phenyl-4:5-dimethylpyrazole. The new base has a pungent odour, but was not obtained in sufficient quantity for purification; on treatment with carbon bisulphide, it yields *dimethylphenyltrimethylenediamine trimethyltrimethylenearilthiocarbamate*,

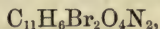


which crystallises in lustrous, white needles, and melts at 210° with slight decomposition.

3:4-Dimethylpyrazole *picrate* forms small needles melting at 155—156°, whilst its 3:5-isomeride melts at 158—159°.

W. J. P.

Some Acids of the Pyrazole Series. By L. BALBIANO and O. SEVERINI (*Gazzetta*, **23**, i, 309—319; 354—360).—1-Phenylpyrazole-4:5-dicarboxylic acid, $\text{C}_3\text{N}_2\text{HPh}(\text{COOH})_2$, is obtained, together with a little oxalic acid, on oxidising 1-phenylmethylethylpyrazole with alkaline permanganate. The new acid crystallises in small, white, pearly laminæ, melting at 231·5° with decomposition; it is soluble in alcohol or hot water, but only sparingly so in ether or cold water. Its *dimethylic* salt forms hard, glossy tables melting at 84·5—85·5°, and is soluble in alcohol or ether, but insoluble in water; it is readily converted into the sodium salt by sodium ethoxide. On treating its alkaline solution with bromine, it yields a *dibromo-derivative*,



which may be extracted from the solution by ether after acidification; it forms small, yellow needles which melt at 197—199° with decomposition, and seems to be accompanied by a monobromo-derivative. On heating for seven hours at 240—255°, the dibromo-derivative loses carbonic anhydride and yields a *dibromophenylpyrazole*, $\text{C}_9\text{N}_2\text{H}_6\text{Br}_2$, which crystallises in white needles melting at 74°, and is soluble in ether and hot alcohol.

1-Phenyl-3:4-dimethylpyrazole is formed by the action of phenylhydrazine on an acidified solution of sodium ethoxide, methylethylacetone, and ethylic formate in ether. It is a pale-yellow oil of sp. gr. = 1·0747 at 0°, boils at 277—278°, and has an aromatic odour; it is soluble in alcohol and ether, insoluble in water, and gives a violet colour with ferric chloride. On oxidation with alkaline permanganate, it gives a mixture of 1-phenyl-3-methylpyrazole-4-carboxylic and

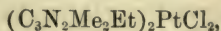
1-phenyl-4-methylpyrazole-3-carboxylic acids, which are separated by crystallisation from dilute alcohol. The former acid is the less soluble, and forms beautiful white needles melting at $191.5-192.5^{\circ}$; it gives a calcium salt which crystallises in small laminæ containing $3\text{H}_2\text{O}$. On heating the acid at $230-250^{\circ}$ for 20 hours, carbonic anhydride is evolved, and 1-phenyl-3-methylpyrazole remains; the constitution of the acid is thus determined. The isomeric acid forms small, white laminæ which melt at $133.5-134.5^{\circ}$; its calcium salt is obtained in crystalline scales containing $2\text{H}_2\text{O}$. On oxidation with alkaline permanganate, both acids give 1-phenylpyrazole-3:4-dicarboxylic acid, which crystallises in white laminæ melting at 200.5° with decomposition; it is soluble in alcohol or boiling water, but only sparingly so in ether. The methylic salt is obtained in long, white needles melting at $74.5-75.5^{\circ}$; it is soluble in alcohol and ether, but insoluble in water.

W. J. P.

Pyrazole-3:5-dicarboxylic Acid. By G. MARCHETTI (*Gazzetta*, 23, i, 567—569).—Buchner and Papendieck (this vol., i, 431) consider that the pyrazole-3:5-dicarboxylic acid obtained by them is not identical with that prepared by Marchetti (this vol., i, 179); their acid melted at $287-290^{\circ}$, whilst that prepared by Marchetti melted at 280° , a temperature, which, by a printer's error, was stated as 180° . The difference of $7-10^{\circ}$ is due to the temperature being corrected in the one case and not in the other. Further, the barium salt crystallises with either 1 or 4 molecules of water. The two acids are therefore identical.

W. J. P.

Platopyrazole Compounds. By L. BALBIANO (*Gazzetta*, 23, i, 524—529; compare Abstr., 1892, 885).—1-Ethyl-3:5-dimethylpyrazole is obtained by heating the silver derivative of 3:5-dimethylpyrazole with ethylic iodide and ether free from alcohol or water in a sealed tube at 100° ; it is a slightly yellowish liquid, soluble in water and alcohol. The platinochloride, $(\text{C}_3\text{N}_2\text{HMe}_2\text{Et})_2\text{H}_2\text{PtCl}_6$, forms small, yellow needles melting at 173° , and is soluble in water or alcohol. On heating it at a little above the melting point, it loses hydrogen chloride, and dichloroplato-1-ethyl-3:5-dimethylpyrazole,



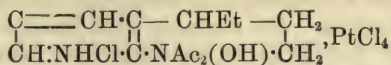
is obtained; this is a bright yellow powder, insoluble in water, and almost insoluble in boiling alcohol. The same compound is obtained on boiling the pyrazole with sodium platinochloride in aqueous solution; the reaction is, however, not complete.

The author has previously observed (Abstr., 1892, 885) that pyrazoles containing a substituted group in the position 4 of the nucleus do not react with sodium platinochlorides to give dichloroplato-derivatives. He now shows that 1-phenyl-4-methylpyrazole is not altered by boiling with aqueous sodium platinochloride; 1-phenyl-3-methylpyrazole, however, under similar conditions, gives rise to dichloroplato-1-phenyl-3-methylpyrazole, $(\text{C}_3\text{N}_2\text{HMePh})_2\text{PtCl}_2$, a light yellow, crystalline powder.

W. J. P.

Pyrazines and Piperazines. A Reply. By C. STOEHR (*J. pr. Chem.* [2], **48**, 191—192).—The author replies to some criticisms by Dennstedt (*ibid.*, **48**, 95) on some remarks contained in the author's recent paper on pyrazines (this vol., i, 486). A. G. B.

Constitution of Nicotine: Acetylnicotine. By A. ÉTARD (*Compt. rend.*, **117**, 170—173).—When nicotine is heated at 150° with acetic anhydride, it is converted into *diacetylnicotine*, a syrupy liquid, which boils, with partial decomposition, at about 330°, and is not affected by alkalis. Its *platinochloride*, $C_{10}N_2H_{14}Ac_2O, HCl, PtCl_4$, crystallises well, and is reconverted into nicotine by hydrogen sulphide. The resistance offered by diacetylnicotine to the action of alkalis seems to indicate that it is an ammonium hydroxide, whilst the removal of the acetyl groups by hydrogen sulphide points to their close connection with nitrogen and platinum. The author suggests the formula $\begin{array}{c} CH:CH:C\cdot CHEt\cdot CH_2 \\ | \\ C=N\cdot C-NH-CH_2 \end{array}$ for nicotine, and the formula



for the platinochloride.

JN. W.

Codeïne. By W. GÖLLICH (*Arch. Pharm.*, **231**, 235—290).—*Codeïne hydrobromide*, $C_{18}H_{21}NO_3, HBr + 2H_2O$, crystallises from alcohol in slender, colourless needles. The hydriodide is deposited from alcohol or ether with $1H_2O$, from water with $2H_2O$, and, contrary to the statement of Anderson (*Annalen*, **77**, 50), becomes anhydrous at 100°. The chromate, $(C_{18}H_{21}NO_3)_2, H_2CrO_4 + 5H_2O$, darkens on exposure to light. The *acetate*, $C_{18}H_{21}NO_3, C_2H_4O_2 + 2H_2O$, crystallises from ethylic acetate, and is extremely soluble in water. The *salicylate*, $C_{18}H_{21}NO_3, C_7H_6O_3$, is amorphous, and readily soluble in alcohol. The *aurochloride* is a yellow, amorphous powder. The platinochloride precipitated from concentrated solutions is, at first, amorphous, but crystallises with $6H_2O$; a second modification, with $4H_2O$, crystallises directly from dilute solution; both compounds become anhydrous on heating at 100—104°. The mercurichloride, $(C_{18}H_{21}NO_3, HCl)_2, HgCl_2 + H_2O$, is deposited in stellate groups of colourless needles. Codeïne does not appear to combine with ethylenic chloride, but, on treatment with ethylenic bromide, an additive compound, $(C_{18}H_{21}NO_3)_2, C_2H_4Br_2$, is formed, which could not be obtained in crystals; it yields a pale yellow, amorphous *platinochloride*.

A comparison of the properties and reactions of v. Gerichsten's crystalline "chlorocodide," $C_{18}H_{20}ClNO_2$ (*Annalen*, **210**, 107), with the amorphous substance prepared by Matthiessen and Wright (*Annalen*, Sup., **7**, 371) shows that they are identical; the latter compound, after purification, crystallises from light petroleum. Chlorocodide gives a yellow coloration with nitric acid, but with sulphuric acid it is almost colourless; Fröhde's reagent gives a yellowish-green colour, changing to blue on heating; Erdmann's reagent, a yellowish-brown,

which becomes red on warming; with vanadic anhydride and sulphuric acid, a yellow coloration is produced, which turns bluish-green on heating.

Chlorocodide aurochloride, $C_{18}H_{20}ClNO_2, HAuCl_4$, is golden yellow and amorphous, and melts at $171-172^\circ$ with decomposition. Chlorocodide is not acted on by tin and hydrochloric acid, by sodium and alcohol, or by silver oxide, but, on heating with alcoholic potash at $120-130^\circ$, it is converted into apocodeine. By the action of water on chlorocodide at $140-150^\circ$, codeine is regenerated.

Sulphocodide, $C_{18}H_{20}NO_2, SO_3H + 5H_2O$, has previously been obtained by Anderson (*loc. cit.*), and is prepared by the action of concentrated sulphuric acid on codeine for 24 hours at ordinary temperatures; it is a neutral compound, crystallising from water in colourless needles, which decompose, without melting, at about 246° . Sulphocodide gives a violet-red coloration on warming with sulphuric acid; the addition of a drop of nitric acid to this solution changes the colour to dark brown and finally to yellow. With concentrated sulphuric acid and cane sugar, a bluish-green coloration is obtained, changing to purple-red on heating. On warming with ferric chloride and concentrated sulphuric acid, it gives an indigo-blue coloration, becoming blood-red on the addition of nitric acid. With concentrated nitric acid alone, at ordinary temperatures, the sulpho-derivative yields a cherry-red coloration which gradually disappears; Erdmann's reagent gives a greenish-blue changing to dull blue; Fröhde's reagent, on warming, a pale reddish-violet; sulphuric acid and vanadic anhydride produce a blue colour.

By the action of dilute sulphuric acid (1 : 1) on codeine at 100° , a compound, termed by Anderson (*loc. cit.*) "amorphous" codeine, is formed, which, on examination, proves to be identical with Merck's pseudocodeine (Abstr., 1891, 1121); the *sulphate* crystallises with $2H_2O$ in tetragonal plates; the *aurochloride*, $C_{18}H_{21}NO_3, HAuCl_4 + 3H_2O$, is amorphous and golden-yellow. Armstrong (*Annalen*, 159, 390) has prepared several of the salts of pseudocodeine described by Merck (*loc. cit.*). Pseudocodeine contains a methoxy-group, but no hydroxy-group, as is shown by its failure to form an acetyl derivative; with the ordinary alkaloidal reagents, it behaves exactly like codeine.

J. B. T.

Quinine, Cinchonidine, and Conchicine. By O. HESSE (*Annalen*, 276, 125-127).—When quinine hydrochloride is heated at 85° with hydrochloric acid of sp. gr. 1.189, the *dihydrochloride*, $C_{20}H_{28}ClN_2O_2, 2HCl$, derived from Comstock and König's hydrochloroquinine is formed; when the salt is dissolved in concentrated sulphuric acid, a sulphonic acid is produced. A base giving a soluble crystalline tartrate is isolated from the mother liquor obtained in the preparation of the last-mentioned dihydrochloride; it is identical either with the author's isoquinine or with Skraup's pseudoquinine.

Hydrochlorocinchonidine resembles hydrochlorapocinchonidine very closely, but whether the two are identical has yet to be decided. A base, *pseudocinchonidine*, is obtained from the mother liquor from the hydrochlorocinchonidine.

Hydrochloroconchinine dihydrochloride yields a sulphonic acid crystallising with $10\text{H}_2\text{O}$ when dissolved in concentrated sulphuric acid; the *platinochloride* of this acid crystallises with $3\text{H}_2\text{O}$, and the *aurochloride* with $1\text{H}_2\text{O}$. The mother liquor from the hydrochloroconchinine dihydrochloride contains α -*isoconchinine*, a crystalline base, the *platinochloride* of which crystallises with $2\text{H}_2\text{O}$, and β -*isoconchinine*, an amorphous base.

A. R. L.

Cinchonine. By O. HESSE (*Annalen*, 276, 88—124).—The author has studied the action of sulphuric and hydrochloric acids on cinchonine, and has obtained 10 of the 16 theoretically possible isomerides.

Cinchonine was prepared from the commercial sulphate by first converting it into the hydrochloride, dissolving the latter in absolute alcohol, and treating the solution with hydrogen chloride, when the *dihydrochloride* separates in lustrous crystals, whilst hydrocinchonine remains dissolved. The *dihydrochloride*, $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O} \cdot 2\text{HCl}$, is readily soluble in water, and has a specific rotatory power in aqueous solution ($p = 3$) $[\alpha]_{\text{D}15^\circ} = +206.1^\circ$.

α -*Isocinchonine* is obtained when cinchonine dihydrochloride is heated at 85° for 48 hours with hydrochloric acid of sp. gr. 1.189; on concentrating the liquid, hydrochlorocinchonine dihydrochloride separates, and when the filtrate is shaken with ammonia and ether, pseudocinchonine is precipitated, and the α -isocinchonine is dissolved by the ether. The base melts at 126° , has a specific rotatory power in alcoholic solution ($p = 3$) $[\alpha]_{\text{D}15^\circ} = +51.6$, and is identical with Comstock and König's isocinchonine and with Jungfleisch and Léger's cinchoniline.

Hydrochlor- α -isocinchonine, $\text{C}_{19}\text{H}_{23}\text{ClN}_2\text{O}$, is obtained, together with hydrochlorapoisocinchonine by the action of fuming hydrochloric acid at 140 — 150° on α -isocinchonine hydrochloride; it melts at 172° , and has a specific rotatory power in alcoholic solution $[\alpha]_{\text{D}15^\circ} = 67.6^\circ$.

β -*Isocinchonine* is obtained by heating α -isocinchonine at 60 — 80° with concentrated sulphuric acid; it is identical with Jungfleisch and Léger's cinchonigine, and is converted into apoisocinchonine when heated at 140 — 150° with hydrochloric acid of sp. gr. 1.125; if, however, it is heated with hydrochloric acid of sp. gr. 1.189 at the same temperature, hydrochlorapoisocinchonine is formed.

Apoisocinchonine is obtained by heating the hydrochloride of α - or β -isocinchonine with hydrochloric acid of sp. gr. 1.125 at 140 — 150° ; it crystallises from aqueous alcohol in white needles, melts at 216° , and has a specific rotatory power ($p = 3$) $[\alpha]_{\text{D}15^\circ} = +166.8$.

Hydrochlorapoisocinchonine is formed when the hydrochloride of α - or β -isocinchonine is heated at 140 — 150° with hydrochloric acid saturated at 0° . When α -isocinchonine is used, the *dihydrochloride* of hydrochlor- α -isocinchonine occurs in the mother liquor. Hydrochlorapoisocinchonine forms white needles, melts at 203° , and has a specific rotatory power in alcoholic solution ($p = 3$) $[\alpha]_{\text{D}15^\circ} = +189.8$. The *dihydrochloride* has a specific rotatory power in aqueous solution ($p = 3$) $[\alpha]_{\text{D}15^\circ} = +172.5$.

Homocinchonine (*Annalen*, **243**, 149) is obtained when cinchonine sulphate is heated at 140° with 25 per cent. sulphuric acid; it forms small, white prisms, melts at 251° , has a specific rotatory power in alcoholic solution ($p = 3$) $[\alpha]_{D15^{\circ}} = +208.9$, and when dissolved in sulphuric acid at the ordinary temperature, yields a mixture of α - and β -isocinchonine, the former predominating.

Pseudocinchonine (see above) forms small, white needles, melts at 252° , and has a specific rotatory power in alcoholic chloroform solution ($p = 3$) $[\alpha]_{D15^{\circ}} = +198.4$.

Hydrochlorocinchonine (Comstock and Königs) is obtained by treating cinchonine hydrochloride with fuming hydrochloric acid at 85° .

Hydrochlorapocinchonine (*Annalen*, **205**, 348) is formed by heating cinchonine or apocinchonine with fuming hydrochloric acid at 140° . The *sulphonic acid*, $C_{19}H_{22}ClN_2O \cdot SO_3H$, is obtained by dissolving the base in concentrated sulphuric acid at the ordinary temperature; it is anhydrous, sparingly soluble in water, and melts at 227° .

Apocinchonine (*Annalen*, **205**, 330) melts at 228° (not 209°), and has a specific rotatory power in alcoholic chloroform ($p = 3$) $[\alpha]_{D15^{\circ}} = +197.5$.

Isoapocinchonine is obtained by heating the dihydrochloride of hydrochlorocinchonine or hydrochlorapocinchonine with water in a sealed tube at 140° ; it forms white prisms, melts at 232 – 234° , and has a specific rotatory power in alcoholic solution ($p = 3$) $[\alpha]_{D15^{\circ}} = +186.2^{\circ}$.

Diapocinchonine is obtained by heating α -isocinchonine at 140 – 150° with hydrochloric acid of sp. gr. 1.125. A determination of the molecular weight by the cryoscopic method showed that it is an isomeride of cinchonine.

Dicinchonine (*Annalen*, **227**, 153) is isomeric and not polymeric with cinchonine.

A. R. L.

Benzoylcinchonine. By E. LÉGER (*Compt. rend.*, **117**, 110–112). —Benzoylcinchonine, prepared by Schützenberger's method, crystallises from absolute ether in colourless and odourless prisms, insoluble in water, but very soluble in aqueous alcohol or aqueous ether, although much less soluble in anhydrous ether. The crystals are anhydrous, soften at 103° , and melt at 105 – 106° (uncorr.). Benzoylcinchonine, unlike cinchonine, is laevogyrate, and at 24° $[\alpha]_D = -22.26^{\circ}$ to -25.35° , the rotatory power, in alcoholic solutions, increasing with the concentration. In acidified alcoholic solutions, the rotatory power diminishes as the proportion of acid increases, and may even change its sign—

1 mol. HCl. $[\alpha]_D = -19.67^{\circ}$		2 mols. HCl. $[\alpha]_D = -16.72^{\circ}$
$\frac{1}{2}$ mol. H_2SO_4 . . . $[\alpha]_D = -17.18^{\circ}$		1 mol. H_2SO_4 . . . $[\alpha]_D = +10.68^{\circ}$

Various salts have been prepared. The basic hydrochloride crystallises in transparent tablets, the normal hydrochloride in needles containing $1C_2H_6O$, the basic hydrobromide in needles containing $1H_2O$, and the platinochloride in golden-yellow needles. The alkyl derivatives as a rule crystallise well.

C. H. B.

Cinchonibine. By E. JUNGLEISCH and E. LÉGER (*Compt. rend.*, 117, 42—44).—The variations observed in the proportions of cinchonifine, apocinchonine, and cinchonibine obtained from cinchonine are due to the fact that cinchonibine splits up into cinchonifine and apocinchonine. When converted into a methochloride, cinchonibine yields apocinchonine methochloride in large, monoclinic prisms containing $4\text{H}_2\text{O}$ and cinchonifine methochloride in prismatic needles containing $2\text{H}_2\text{O}$.

When cinchonibine is converted into basic succinate, it yields large, hexagonal crystals, which contain $6\text{H}_2\text{O}$, and are very different in appearance from cinchonifine succinate, but crystallographically identical with the succinate prepared from pure apocinchonine. Further, if increasing quantities of cinchonifine are added to the apocinchonine, the succinate always has the same form, and it follows that basic apocinchonine succinate has the power of taking up large quantities of cinchonifine succinate without any change in appearance. If a mixture of equal weights of cinchonifine and apocinchonine is converted into basic succinate, and the latter is decomposed by an alkali, it yields cinchonibine.

Cinchonibine can no longer be regarded as a true isomeride of cinchonine. It seems, however, to be a definite compound of cinchonifine and apocinchonine in equal proportions, and has the same properties, and, notably, the same rotatory power, when prepared by several different methods. Under the microscope, the crystals seem to be homogeneous. The compound remains unchanged when dissolved in a small quantity of alcohol, but splits up if a large quantity of the solvent is used. The rotatory power of cinchonibine solutions is the mean of the rotatory powers of cinchonifine and apocinchonine.

C. H. B.

Hyoscyne and Oscine. By O. HESSE (*Annalen*, 276, 84—86).—The aurochloride obtained from commercial hyoscyne hydriodide has the composition $\text{C}_{17}\text{H}_{21}\text{NO}_4 \cdot \text{HAuCl}_4$, and melts at 198° . As thus prepared, it appears to contain a trace of an unknown alkaloid, which does not, however, alter its composition.

The formula of benzoyloscine was erroneously given (*Abstr.*, 1892, 1498) as $\text{C}_{15}\text{H}_{17}\text{NO}_4$; it should be $\text{C}_{15}\text{H}_{17}\text{NO}_3$. The formula of oscine aurochloride (*loc. cit.*) requires similar alteration. When benzoyloscine is warmed with hydrochloric acid, it decomposes into oscine and benzoic acid.

A. R. L.

Organic Bases in the Tubers of *Stachys tubrifera*. By A. v. PLANTA and E. SCHULZE (*Arch. Pharm.*, 231, 305—313; compare this vol., ii, 53).—It has been previously shown that the tubers of *Stachys tubrifera* contain glutamine and tyrosine (*Abstr.*, 1890, 1183); two other nitrogenous bases have now been isolated, one of which occurs in very small quantity, and has not hitherto been investigated. The second compound, $\text{C}_7\text{H}_{13}\text{NO}_2$, which it is proposed to term *stachydrine*, is separated by means of auric chloride and purified by the help of the platinochloride; it is deposited from dilute alcohol in colourless, transparent crystals containing water of crystallisation. The base in aqueous solution is neutral to litmus, and, like the first

compound, is indistinguishable from betaine by the ordinary alkaloïdal reagents. The *hydrochloride*, $C_7H_{13}NO_2.HCl$, crystallises from water or absolute alcohol in large, colourless prisms. The *platinochloride* crystallises with $2H_2O$ in flat, orange-red, rhombic prisms, $a : b : c = 0.6082 : 1 : 0.8277$. The *aurochloride* is deposited from water in small, yellow prisms. The *mercurochloride* and *nitrate* are colourless and crystalline. The *picrate* forms small, yellow prisms.

J. B. T.

Cryoscopy of Albumose and Peptone. By A. SABANÉEFF (*J. Russ. Chem. Soc.*, 25, 11—23).—A cryoscopic investigation of deutero-albumose from albumin, in aqueous solution, led to a molecular weight of about 3200; this number varied very little with the concentration of the solution. The molecule would thus seem to contain 2 atoms of sulphur. Proto-albumose has a somewhat similar molecular weight. The molecular weight of albumin-peptone (amphopeptone) is less than 400, increasing considerably with the concentration. The molecule of peptone contains no sulphur.

J. W.

Nucleïnic acid. By A. KOSSEL and by J. HORBACZEWSKI (*Chem. Centr.*, 1893, i, 787—788; from *Arch. Physiol.*, 1893, 107—115 and 157—164).—Nucleic acid from yeast, on treatment with dilute acids, is resolved into a number of basic substances, and a compound which appears to be a pentose; it forms a *phenylglucosazone*, melting at $204-205^\circ$, and a *phenylhydrazone*, melting at 150° . *Plasmic acid*, $C_{15}H_{25}N_6P_6O_{30}$, is formed by the action of alkalis on nucleic acid; on treatment with dilute acids, it yields a nitrogenous substance which has not been investigated, nucleic bases, guanine or adenine, and a compound of phosphorus which, in spite of Liebermann's statement to the contrary, is not metaphosphoric acid. The assertion that the nucleic acids are compounds of metaphosphoric acid and albumin also lacks foundation, as is shown by a comparison of the natural and artificial products. The part played by nucleic acid in the economy of the cell is discussed; it is probably actively engaged in the destruction of pathogenic micro-organisms and their products.

Horbaczewski's experiments on the formation of uric acid from spleen extract (Abstr., 1891, 1340) have been questioned, but he shows that the uric acid produced was pure and free from xanthine; the two compounds can be readily separated by precipitating the acid with ammonium chloride or hydrochloric acid.

J. B. T.

Organic Chemistry.

Determination of Stereoisomerides. By E. NICKEL (*Zeit. physikal. Chem.*, **12**, 275—279).—The author gives a convenient graphical method for determining the number and optical nature of stereoisomerides with a given number of asymmetric carbon atoms.

J. W.

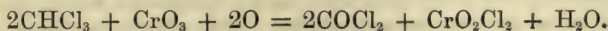
Köhnlein's Method of preparing the Paraffins: Properties of Propane. By L. MEYER (*Ber.*, **26**, 2070—2073).—When secondary hexylic iodide, prepared from mannitol, is treated with aluminium chloride in a sealed tube, according to Köhnlein's method (*Ber.*, **16**, 560), ethane and butane are produced. The hexane chain has therefore been broken at the carbon atom with which the iodine is combined. Experiments are proceeding in order to ascertain whether this is a general reaction of the secondary iodides.

Propane can easily be liquefied at the atmospheric pressure by means of solid carbonic anhydride, and boils at -38° to -39° . The critical temperature is about 102° , the critical pressure being about 59 atmospheres. The following tables show the vapour pressure of the liquid and its specific gravity at various temperatures.

Vapour pressure.		Vapour pressure.	
Temp.	Metres.	Temp.	Metres.
-33°	1.43	$+5.5^{\circ}$	4.53
-19	2.08	12.5	5.41
-15	2.41	22.0	7.6
-11	2.78	34.0	10.5
-5	3.16	53.0	18.9
-2	3.71	85.0	35.0
$+1$	3.89	103.0	45.6
Temp.....	0°	6.2°	11.5°
Sp. gr.	0.535	0.526	0.519
			0.512

A. H.

Oxidation of Chloroform with Chromic acid, and Preparation of Carbon Oxychloride from Carbon Tetrachloride. By H. ERDMANN (*Ber.*, **26**, 1990—1994).—This paper opens with a short but valuable *résumé* of the subject. The oxidation of chloroform with sulphuric acid and potassium dichromate was studied by Emmerling and Lengyel in 1869; these chemists found but a small amount of carbon oxychloride among the products, and they incorrectly interpreted the reaction, inasmuch as they believed that chlorine is formed. The author states that the reaction is the following.



Schützenberger showed, in 1869, that carbon oxychloride is obtained in good yield by the action of sulphuric anhydride on carbon tetra-

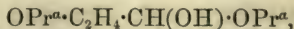
chloride. The following method of preparing carbon oxychloride is described by the author. Carbon tetrachloride (100 grams) is heated to boiling on a water bath in a flask furnished with a vertical reflux condenser; 80 per cent. anhydrosulphuric acid (120 c.c.) is run in drop by drop down the condenser, so that each drop comes into intimate contact with the ascending vapour of the carbon tetrachloride. The evolved carbon oxychloride passes, by a tube fused at right angles to the upper portion of the condenser tube, through concentrated sulphuric acid contained in a wash bottle (which is kept in water during the experiment), and thence to a Hofmann's receiver surrounded by a freezing mixture. When all the anhydrosulphuric acid has been run in, the globular flask is boiled over a free flame for five minutes. The yield of crude carbon oxychloride is 90 per cent. of the theoretical. It is rectified, the boiling flask being heated by the hand. The accompanying product is a mixture of pyrosulphuryl chloride, $S_2O_5Cl_2$, and chlorosulphonic acid, SO_3HCl ; this mixture boils at $130-150^\circ$, and forms a valuable sulphonating agent. A. R. L.

Acrylonitrile. By MOUREU (*Bull. Soc. Chim.*, [3], 9, 424—427).—Acrylamide is distilled with twice its weight of phosphoric anhydride at $150-250^\circ$; about 30 per cent. of the theoretical yield of acrylonitrile is obtained. Its vapour density is 1.84. It is a colourless, mobile liquid soluble in water, having a feeble odour of hydrogen cyanide, and has no irritant action on the eyes; the sp. gr. = 0.843 at 0° . It boils at 78° , a temperature below that of the boiling points of acetonitrile (84°) and propionitrile (97°). It combines with bromine to form $\alpha\beta$ -dibromopropionitrile, a liquid of sp. gr. 2.161 at 0° , insoluble in water, and intensely irritant in its action on the eyes.

β -Hydroxypropionitrile, although more stable than the corresponding acid, yields acrylonitrile when distilled with phosphoric anhydride. W. T.

Action of Iodine on Sodium Propoxide. By A. KESSLER (*J. pr. Chem.*, [2], 48, 236—240).—The action of iodine on sodium propoxide is similar to its action on sodium isobutoxide.

The propyl derivative of hydroxypropaldehyde,



is obtained by gradually adding iodine to sodium propoxide, and cooling the mixture in ice-cold water; the product is then neutralised with tartaric acid, and fractionally distilled, when the ethereal derivative is precipitated as an oil, and is purified by distillation under diminished pressure. It distils at $111-114^\circ$ under 26—28 mm. pressure, and is a colourless, highly refractive liquid having a characteristic odour. When heated in a sealed tube with acetic acid, it is converted into propylic acetate and a compound which the author believes to be hydroxypropaldehyde. This shows no fixed boiling point, the thermometer rising steadily from 100° to 170° ; it has a characteristic odour, and quickly reduces ammoniacal silver solution.

A volatile acid was also obtained by the action of iodine on sodium propoxide, but it was not examined.
E. C. R.

Myricyl Alcohol. By A. GASCARD (*J. Pharm.*, [5], 28, 49—54).—Myricyl alcohol has been prepared by the author from gum-lac, carnauba wax, and beeswax, and the product found to be identical in each case. Myricyl alcohol melts at 88° , and is a white solid, very slightly soluble in cold benzene, ether, or light petroleum, easily soluble in hot benzene, alcohol, and chloroform. On cooling the solutions, microscopic crystals are deposited, of which the form varies with the solvent; alcohol gives large, soft needles, benzene harder, feathery aggregates of nacreous lustre, and chloroform more aggregated forms.

Myricylic acetate is soluble in alcohol, benzene, and chloroform. It melts at 73° . Myricylic laurate (m. p. $69-70^{\circ}$) is less soluble in the same solvents. Myricylic palmitate (m. p. 75°), stearate (m. p. 78°), and arachidate (m. p. 84°) are insoluble in hot alcohol, but soluble in benzene. Myricylic cerotate (m. p. 87°) and melissate (m. p. 92°) are insoluble in boiling alcohol, and myricylic oleate (m. p. 65°) is but slightly soluble in alcohol. Myricylic benzoate crystallises from ether in fine plates melting at 70° . It is soluble in hot alcohol and cold benzene. Normal myricylic oxalate (m. p. 91°) is insoluble in boiling alcohol, and crystallises from benzene. Hydrogen myricylic phthalate is soluble in hot alcohol; the normal salt is insoluble in alcohol, but soluble in benzene. Both melt at 79° .
W. T.

Raffinose and its Decomposition Products. By A. AULARD (*Bied. Centr.*, 1893, 703—704).—The best method for estimating raffinose in beet sugar is that introduced by Clerget with Herzfeld's modifications.

In the first products, neither Aulard nor Herzfeld could detect raffinose, and in the after products it was only present in small quantities.

The action of raffinose as affecting the formation of molasses cannot be expressed by a coefficient for the simple reason that it does not appear to exert any but a favourable influence on the crystallisation of saccharose, and it only appears in the final product, which consists of raffinose, saccharose, a few salts, and much organic matter.

Further, Aulard considers that, of all salts, organic calcium salts influence the formation of molasses least, and that crystallisation is not dependent on the presence of salts generally, but on the viscosity of the solution, which is itself limited by the presence of soluble organic calcium salts.
E. W. P.

Combination of Iodine with Starch. By G. ROUVIER (*Compt. rend.*, 117, 281—282).—If an aqueous solution of starch is gradually mixed with iodine, it is found that iodine remains in the free state as soon as its proportion exceeds that required by the formula $(C_6H_{10}O_5)_{16}I_3$. It would seem, therefore, that there are three definite compounds of starch with iodine, $(C_6H_{10}O_5)_{16}I_2$, $(C_6H_{10}O_5)_{16}I_3$, $(C_6H_{10}O_5)_{16}I_4$. (Compare Abstr., 1892, 575, 801, and 1171.)

C. H. B.

Dextrin. By V. GRIESSMAYER (*J. pr. Chem.*, [2], **48**, 225—230).—After reviewing the results obtained by other workers, the author concludes that in the reactions of the mash-tub a part of the molecule of the soluble starch is converted into amylopectin, and of the six amylin groups of the latter, four are then converted into maltose (or isomaltose); the remainder is maltodextrin.

E. C. R.

Occurrence of Betaine and Choline in the Sprouts of Barley and Wheat. By E. SCHULZE and S. FRANKFURT (*Ber.*, **26**, 2151—2155).—The authors have succeeded in isolating and identifying betaine and choline from the sprouts, or young seedlings, of barley (malt combs) and wheat. The method adopted was to extract the sprouts with water, treat the extract with lead acetate, and, after filtering, to precipitate the bases with phosphotungstic acid. The precipitate was then treated with milk of lime, the solution filtered, treated with carbonic anhydride, again filtered, neutralised with hydrochloric acid, and concentrated to a syrup. The hydrochlorides were extracted with hot alcohol, precipitated with an alcoholic solution of mercuric chloride, and the mercurichlorides separated by repeated crystallisation from water; or after crystallising them once or twice, the mercury was removed with hydrogen sulphide, and the hydrochlorides separated by means of cold absolute alcohol, in which choline hydrochloride dissolves, whilst betaine hydrochloride does not.

C. F. B.

Oxidation of the Two Trithioacetaldehydes. By E. BAUMANN (*Ber.*, **24**, 2074—2079; compare Abstr., 1890, 25).—The oxidation of the stereoisomeric trithioacetaldehydes by means of potassium permanganate in the presence of sulphuric acid leads to the production of a disulphone sulphide, $C_6H_{12}S_3O_4$, and a trisulphone, $C_6H_{12}S_3O_6$, the products obtained from α - and β -trithioacetaldehyde being identical in every respect. The isomerism of these substances is therefore of a nature different from that of fumaric and maleic acids, since the latter are converted by oxidation into optically isomeric products. Guareschi (Abstr., 1884, 294), who has also examined the action of potassium permanganate on trithioacetaldehyde, used impure material, and did not succeed in completely separating the products formed. The *disulphone sulphide* crystallises in long, transparent prisms or needles, which are odourless, and melt at 283—284°. It is the symmetrical trimethyl substitution product of the trimethylenedisulphone sulphide described by Camps (Abstr., 1892, 592), and has the formula $SO_2 < \begin{smallmatrix} CHMe-S \\ CHMe \cdot SO_2 \end{smallmatrix} > CHMe$. It is moderately soluble in hot alcohol and acetic acid, but almost insoluble in chloroform, benzene, or ether. It contains one atom of hydrogen replaceable by metals, and is readily soluble in alkalis, but does not yield crystalline salts. It dissolves in concentrated acids on warming, and is reprecipitated by the addition of water. Fuming nitric acid partially oxidises it with production of a small amount of sulphuric acid, whilst a hot solution of potassium permanganate in the presence of dilute sulphuric acid slowly converts it into the trisulphone. The

properties of the latter substance will form the subject of a later publication. A. H.

Citronellaldehyde. By F. W. SEMMLER (*Ber.*, **26**, 2254—2258; compare *Abstr.*, 1891, 539).—*Citronellaldoxime*, $C_{10}H_{18}NOH$, boils at $135\text{--}136^\circ$ under 14 mm. pressure; the sp. gr. is 0.9055 at $20^\circ/20^\circ$, and the molecular refraction 52.67 .

The *nitrile of citronellaldehyde*, $C_{10}H_{17}N$, obtained by boiling the oxime with acetic anhydride, boils at 94° under 14 mm. pressure; the sp. gr. is 0.8645 at $20^\circ/20^\circ$, and the molecular refraction 47.43 .

Citronellic acid, $C_{10}H_{18}O_2$, is most easily obtained by treating the nitrile with alcoholic potash. It boils at 143.5° under 10 mm. pressure, and at 257° under atmospheric pressure; the sp. gr. is 0.9308 at $20^\circ/20^\circ$, and the molecular refraction 49.60 .

Dihydroxycitronellic acid $C_{10}H_{18}O_2(OH)_2$, is obtained by treating the preceding acid in very dilute solution with potassium permanganate at 0° . The *silver* salt is a white powder. The author was unable to obtain a lactone from this acid.

Citronellapimelic acid, $C_7H_{12}O_4$, is obtained by oxidising the preceding acid with chromic acid mixture. It crystallises in needles, and melts at $82\text{--}83^\circ$. The *silver* salt is a white powder insoluble in water.

The author concludes that citronellaldehyde (citronellal) has the constitution $CHO \cdot CHMe \cdot [CH_2]_3 \cdot CH : CMe_2$. E. C. R.

Ketonic Compound from Tartaric acid. By E. MULDER (*Rec. Trav. Chim.*, **12**, 51—100; compare *Abstr.*, 1890, 595; 1891, 830; 1892, 965).—In combining with ethylic chloride, ethylic disodiotartrate resembles ethylic sodacetoacetate (compare Nef, *Abstr.*, 1892, 141). The copper derivative, $C_{16}H_{24}CuO_{11}$ (*Abstr.*, 1892, 965) seems to be anhydrous; it begins to decompose at 115° , and to melt at 130° . When dissolved in absolute alcohol, and treated with a slight excess of alcoholic hydrogen sulphide, a crystalline *ketone*, $C_{16}H_{24}O_{10}$, is obtained; the aqueous solution of this substance gives a cherry-red coloration with ferric chloride, a precipitate with barium hydroxide, and a crystalline compound with phenylhydrazine. When the copper derivative is dissolved in dilute hydrochloric acid, and treated with phenylhydrazine, an oily compound is obtained.

The author was unable to prepare a crystalline copper compound from the insoluble portion of the product of the action of ethylic chloride on ethylic disodiotartrate.

Ethylic disodioracemate reacts with ethylic chloridé, forming a soluble and an insoluble compound; the *copper* derivative obtained from the former has the same composition as that from ethylic disodiotartrate (dextro-); it, follows, therefore, that both the dextro- and lævo-tartaric acid derivatives react in an analogous manner.

A provisional study of the barium derivatives of the soluble and insoluble products of the action of ethylic chloride on ethylic disodiotartrate has revealed nothing definite up to the present; the author finds that the barium derivative of the insoluble portion of the product gives with hydrochloric acid and phenylhydrazine a

crystalline compound which resembles E. Fischer's pyruvic hydrazone, but is not identical with it.

Copper ethoxide is prepared by treating a solution of sodium ethoxide in absolute alcohol (pure) with anhydrous cupric chloride; it is a gelatinous compound of an indigo-blue colour.

An alcoholic solution of ethylic disodiotartrate yields a blue solution with cupric chloride, and gives no precipitate with anhydrous ferric chloride.

Copper pyruvate has the composition $(C_3H_3O_3)_2Cu + H_2O$, assigned to it by Berzelius (*Annalen*, 36, 24); it is, however, crystalline.

The author was unsuccessful in preparing hydvric acid by the method described by Böttinger (*Annalen*, 208, 131), namely, treatment of basic barium pyruvate with carbonic anhydride.

By the action of sodium ethoxide on ethylic succinate in an atmosphere of hydrogen under reduced pressure, ethylic sodium succinate appears to be formed, but the tendency for the production of the closed chain compound, sodium succinosuccinate, is so great, that the alcohol, which probably combines with the succinate initially formed, cannot be eliminated.

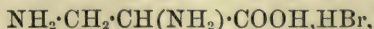
A. R. L.

Ethylic Orthoformates. By J. WALTER (*J. pr. Chem.*, [2], 48, 231—235).—Ethylic orthoformate may be obtained by adding a mixture of chloroform and alcohol to an aqueous solution of sodium hydroxide. The best yield was about 19 per cent. of the theoretical.

The author could not obtain a condensation product from ethylic orthoformate and diphenylamine. Trimethyltriphenylparaleucaniline is obtained by heating methyldiphenylamine, ethylic orthoformate, and zinc chloride on the water bath.

E. C. R.

Diamidopropionic acid. By E. KLEBS (*Ber.*, 26, 2264—2267).—*Diamidopropionic acid hydrobromide*,



is obtained by heating $\alpha\beta$ -dibromopropionic acid with 20 molecular proportions of an aqueous solution of ammonia saturated at 0° . It crystallises in needles, darkens at 225° , melts at 228 — 230° with decomposition, shows a slight acid reaction with litmus, and is soluble in 12.5 parts of water at 20° .

Copper diamidopropionate, is obtained by treating the hydrobromide with lead hydroxide, then with hydrogen sulphide, and adding to the warm alkaline filtrate freshly-prepared copper hydroxide. It crystallises, with $4H_2O$, in violet-blue, monoclinic forms, and is dehydrated with difficulty. The dry salt absorbs water very energetically.

Diamidopropionic acid hydrochloride, obtained by treating the hydrobromide with lead hydroxide and then adding hydrochloric acid, is a white, crystalline powder, darkens at 220° , melts at 225° with decomposition, and is soluble in 11.57 parts of water at 20° . The

free acid is obtained by adding silver oxide to a solution of the hydrochloride, precipitating the dissolved silver with hydrogen sulphide, and evaporating the filtrate in a vacuum. It is a strongly alkaline syrup, solidifies when mixed with absolute alcohol and cooled, and is very hygroscopic.

E. C. R.

Preparation of Normal Caproic and Hexylic acids. By J. TRIPIER (*Compt. rend.*, 117, 282—284).—When castor oil and other vegetable oils are treated with nitric acid, the yield of heptylic acid is very small, and the result is not appreciably affected by variations in the concentration of the acid. Better results can, however, be obtained by using a mixture of nitric and sulphuric acids. 2000 c.c. of nitric acid is mixed with 500 c.c. of sulphuric acid, previously diluted with 2000 c.c. of water, and to this mixture is added 1000 c.c. of castor oil. The liquid is then heated until the reaction commences, and again after the effervescence has ceased, the product being distilled until about 2000 c.c. has passed over. After separation of the acid by means of a separating funnel, the 2000 c.c. of aqueous solution is treated with a further quantity of 500 c.c. of sulphuric acid and 2000 c.c. of nitric acid, in order to complete the oxidation.

Under these conditions, 1000 c.c. of castor oil yields about 500 c.c. of non-volatile bibasic acids, and 250 c.c. of volatile acids of the acetic series. The latter are mixed with a considerable proportion of normal heptylonitrile, but otherwise consist solely of normal hexylic and heptylic acids, in the proportion of 1 part of the former to 3 parts of the latter.

C. H. B.

Di- γ -amidodipropylacetic acid and Octahydro-1:1'-naphthyridine. By A. REISSERT (*Ber.*, 26, 2137—2144).—Using Gabriel's synthetic method (*Abstr.*, 1890, 1129; 1891, 948), ethylic di- γ -phthalimidopropylmalonate, $C(CH_2 \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot O_2N)_2(COOEt)_2$, has been prepared from sodium ethoxide, ethylic malonate, and γ -bromopropylphthalimide. When heated at 180° with hydrochloric acid, it is decomposed into phthalic acid, ethylic chloride, carbonic anhydride, and di- γ -amidodipropylacetic acid, $CH(CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2)_2 \cdot COOH$; this acid, when distilled under atmospheric pressure, yields octahydro-naphthyridine.

Ethylic di- γ -phthalimidopropylmalonate crystallises in soft, white needles, which melt at 155.5° (corr.). When boiled with strong aqueous potash, it is hydrolysed, and, if the product is neutralised and then shaken with benzoic chloride and soda, *di- γ -lenzamidodipropylmalonic acid*, $C(CH_2 \cdot CH_2 \cdot CH_2 \cdot NHBz)_2(COOH)_2$, is obtained; this forms a white, sandy, crystalline mass, which softens when heated, and finally melts at 188 — 189° . The *silver*, $C_{23}H_{24}N_2O_6Ag_2$, and *barium*, $C_{23}H_{24}N_2O_6Ba$, *salts* are colourless, the latter crystalline. *Di- γ -amidodipropylacetic acid* is obtained, as above described, as the *hydrochloride*, with $2HCl$, a white, hygroscopic substance. This is converted, by shaking with benzoic chloride and soda, into *di- γ -benzamidodipropylacetic acid*, which forms dull, white crystals, and yields a *silver salt*, $C_{22}H_{25}N_2O_4Ag$. *Di- γ -amidodipropylacetic acid* is itself obtained from

the hydrochloride by means of silver oxide; it forms a yellow oil, which distils unchanged under 35—40 mm. pressure. *Octohydronaph-*

tyridine, $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{NH}\cdot\text{C}\cdot\text{N}\cdot\text{CH}_2 \end{array} > \text{CH}_2$, obtained from it as described above, forms a yellowish oil, probably slightly impure; the *platinochloride*, $(\text{C}_8\text{H}_{11}\text{N}_2)_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in orange needles, and melts at 227° (uncorr.). C. F. B.

Action of Acrylic Chloride on Alcohols and Phenols. By MOUREU (*Bull. Soc. Chim.*, [3], 9, 415—417).—Ethereal salts of β -chloropropionic acid are formed by the action of acrylic chloride on alcohols and phenols. The products are identical with the ethereal salts prepared by the direct action of the alcohols on β -chloropropionic acid. Although hydrogen chloride is not evolved by the action of acrylic chloride on alcohols, the chloride itself does not absorb hydrogen chloride.

Methylic β -chloropropionate boils at 148° , and has a sp. gr. of 1.198 at 0° . Ethylic β -chloropropionate boils at 162° . Propylic β -chloropropionate has a very sweet and agreeable odour, a sp. of 1.092 at 0° , and boils at 179 — 181° . Isobutylic β -chloropropionate boils at 191 — 193° , and has a sp. gr. of 1.066 at 0° .

Phenyllic β -chloropropionate is formed by the action of acrylic chloride (5 grams) on phenol (6 grams). The phenol is melted and mixed with the chloride, and, after 24 hours' contact, the product is distilled. A liquid of the composition $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{COOPh}$ passes over between 154° and 157° under a pressure of 30 mm. W. T.

Acrylic Anhydride. By MOUREU (*Bull. Soc. Chim.*, [3], 9, 413—415).—Finely powdered sodium acrylate (22 grams) is mixed with a little vaseline, and acrylic chloride (20 grams) added drop by drop, keeping the well-agitated mass cool. The reaction is completed by heating for half an hour on the water bath, and the product is then distilled under reduced pressure.

Acrylic anhydride, $(\text{CH}_2\cdot\text{CH}\cdot\text{CO})_2\text{O}$, decomposes partially on distillation, even in a vacuum. It is a colourless liquid of sharp odour; its action on the eyes is less violent than that of acrylic chloride; sp. gr. 1.094 at 0° . It is easily decomposed by water, and takes up the theoretical quantity of bromine at the ordinary temperature. It slowly decomposes, yielding a white, solid mass. W. T.

Constitution of the Unsaturated Acids obtained by boiling the Unsaturated $\beta\gamma$ -Acids with Soda. By R. FITTIG (*Ber.*, 26, 2079—2081).—The author has compared the acid produced by boiling $\beta\gamma$ -pentylenic acid (ethylidenepropionic acid) with soda with the $\alpha\beta$ -pentylenic acid (propylideneacetic acid) prepared by Komnenos from propaldehyde and malonic acid; this reaction always yields a certain amount of the $\beta\gamma$ -acid, in addition to the $\alpha\beta$ -isomeride. In order to separate the two acids, their barium salts are repeatedly extracted with alcohol, and the more soluble portion used for the preparation of the

$\alpha\beta$ -acid. The liberated acid is then warmed with sulphuric acid, which converts the $\beta\gamma$ -derivative into valerolactone, whilst the pure $\alpha\beta$ -acid is left.

This substance, which has not previously been obtained pure, solidifies, on cooling, in large plates or prisms, melting at 8–9°. It forms a characteristic *dibromide*, which crystallises well, is very readily soluble in light petroleum, benzene, &c., and melts at 55–56°. The acid also combines with hydrogen bromide to form *β -bromovaleric acid*, which is slightly soluble in light petroleum, and crystallises in large, transparent, well-developed, monosymmetric prisms, melting at 59–60°.

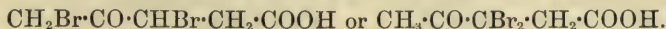
The acid obtained by boiling $\beta\gamma$ -pentylenic acid, prepared from methylparaconic acid, with a 10 per cent. solution of soda has precisely the same properties, and forms the same additive products.

The three isomeric pentylenic acids and their dibromides are now all known in the pure state, and differ so greatly in properties as to be easily distinguished.

	B. p.	M. p. of dibromide.
$\alpha\beta$ -Pentylenic acid, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{COOH}$ (propylideneacetic acid).....	201°	56°
$\beta\gamma$ -Pentylenic acid, $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$ (ethylidenepropionic acid)	194°	65°
$\gamma\delta$ -Pentylenic acid, $\text{CH}_2\cdot\text{CH}:\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ (allylacetic acid).....	187°	58°

The production of the $\beta\gamma$ -acid, in addition to the $\alpha\beta$ -derivative, by the condensation of propaldehyde with malonic acid, renders it probable that β -hydroxyvaleric acid is formed as an intermediate product, and then decomposes in the usual way, with formation of both isomerides. A. H.

Constitution of Dibromolevulinic acid. By L. WOLFF (*Ber.* 26, 2216–2221; compare *Abstr.*, 1891, 416).—Dibromolevulinic acid has been shown to have one of the two formulæ



The oxidation of the acid by means of concentrated nitric acid proves that the former of these represents its constitution, the products formed being dibromodinitromethane and monobromosuccinic acid; oxalic acid and fumaric acid, both probably derived by a secondary reaction from the latter, being also produced. Dibromodinitromethane, $\text{CBr}_2(\text{NO}_2)_2$, has been previously obtained by Losanitsch (*Ber.*, 15, 473; 16, 51), by the oxidation of tribromaniline and ethylenic dibromide, in both of which compounds only one bromine atom is combined with a single carbon atom. It is a very volatile, faintly yellowish-green oil, which solidifies to white, lustrous plates, melting at 10°. It is somewhat soluble in water, more readily in dilute acids, and liberates iodine from solutions of potassium iodide and hydriodic acid. On treatment with caustic potash solution, it is converted into the explosive yellow potassium

salt, $\text{CBrK}(\text{NO}_2)_2$, described by Losanitsch; his statement that a solution of this salt, when decomposed by dilute sulphuric acid, yields the original dibromodinitromethane and not the monobromo-compound as might have been expected, has been confirmed. This reaction shows that monobromodinitromethane must be a very unstable substance, and throws some light on the formation of the dibromo-derivative by the oxidation of a group only containing one bromine atom.

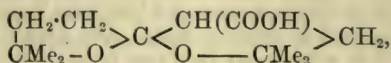
In connection with the decomposition of dibromolevulinic acid by boiling with water, the constitution of tetric and pentic acids is being further investigated. The following results have already been obtained. On oxidation, tetric acid yields a considerable amount of diacetyl, so that this method might well be employed for the preparation of the latter. The acid is decomposed by water at 200° , among the volatile, neutral substances formed, being one which boils at $155\text{--}156^\circ$, and has the composition $\text{C}_4\text{H}_8\text{O}_2$; this substance shows all the properties of a ketonic or aldehydo-alcohol, and, on oxidation, yields propionic acid. Its formula is, probably, $\text{COEt}\cdot\text{CH}_2\cdot\text{OH}$.

Tetric acid is converted by the action of concentrated nitric acid, or, better, of nitrous acid, into a white, crystalline compound, a series of colour changes, such as occur in the formation of a pseudonitrole, taking place. This substance has the formula $\text{C}_5\text{H}_5\text{O}_3\cdot\text{NO}$, is very slightly soluble in the ordinary solvents, melts at 131° with decomposition, and gives Liebermann's reaction. It has no longer the character of an acid, and is decomposed by boiling water or alkalis. The compound may be either a nitroso-derivative or a salt of nitrous acid. A. H.

Action of Sodium Ethoxide and Ammonia on Isocapro-lactone. By T. STRÖM (*J. pr. Chem.*, [2], 48, 209—222).—Isocapro-lactone is obtained in theoretical quantity by distilling terebic acid in an apparatus so arranged that for every drop of the distillate that runs into the receiver, 7—8 drops run back into the distilling flask. The distillate is then subjected to a second distillation.

Diisohexolactone, $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CMe}_2-\text{O} \end{array} > \text{C} : \text{C} < \begin{array}{c} \text{CH}_2\cdot\text{CMe}_2 \\ | \\ \text{CO}-\text{O} \end{array}$, is obtained by heating sodium ethoxide with isocapro-lactone dissolved in absolute alcohol on the water bath for eight hours. The product, which contains an acid, is dissolved in ether, and the acid extracted from the solution by shaking with aqueous potassium carbonate. It separates from ether in large, colourless crystals, and from alcohol in needles, melts at $103\cdot8^\circ$, is volatile with steam, and is insoluble in cold sodium hydroxide, but slowly dissolves when heated. When heated with water, or with dilute hydrochloric or sulphuric acid, it is slowly converted into tetramethyloxetone.

Tetramethyloxetonecarboxylic acid (diisohexonic acid),



is obtained, together with tetramethyloxetone, by boiling the preceding compound with dilute sodium hydroxide. It crystallises from ether in short, thick crystals, and from water in needles containing $\frac{1}{2}\text{H}_2\text{O}$, which melt at 81° . The anhydrous acid melts at 108° . When boiled with water or dilute acids, or when heated above its melting point, it is converted into tetramethyloxetone and carbonic anhydride. The *calcium salt*, $(\text{C}_{12}\text{H}_{19}\text{O}_4)_2\text{Ca}$, is more soluble in cold than in warm water, and crystallises from alcohol in small needles. The *barium salt* crystallises in needles, and is soluble in alcohol. The *silver salt* is obtained as a white, voluminous precipitate, is not very stable, and when boiled with water, decomposes into carbonic acid, tetramethyloxetone, and metallic silver.

Tetramethyloxetone, $\text{C}\left(\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{O}-\text{CMe}_2 \end{array}\right)_2$, is best obtained by boiling the product of the action of sodium ethoxide on isocapro lactone with water, acidifying with hydrochloric acid, and subjecting the mixture to steam distillation. It is a colourless liquid, boils at 178.5° , has an odour resembling that of peppermint, and is more soluble in cold water than in water at $35-90^\circ$. It is not altered by dilute alkalis or acids, and slowly reduces ammoniacal silver solution.

γ -Hydroxyisocaproamide, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CONH}_2$, is obtained by saturating a solution of isocapro lactone in absolute alcohol at 0° with dry ammonia, and heating the mixture for four hours in a sealed tube at 100° , or by shaking the lactone for 24 hours with an aqueous solution of ammonia saturated at 0° . It crystallises in large tablets or beautiful lustrous plates, and melts at 101° . It is not altered by cold sodium hydroxide, but, on heating, ammonia and sodium hydroxyisocaproate are formed. When heated with hydrochloric acid, the lactone and ammonium chloride are formed. When heated in a paraffin bath at 147° , it is decomposed into the lactone and ammonia.

Ammonium γ -hydroxyisocaproate is obtained by adding ammonium sulphate to a solution of barium γ -hydroxyisocaproate and evaporating the filtrate over sulphuric acid. It crystallises from absolute alcohol with partial decomposition, melts at 127° , and at higher temperatures is converted into the lactone, ammonia, and water.

E. C. R.

Aticonic acids, New Isomerides of the Itaconic, Citraconic, and Mesaconic acids. By R. FITTIG (*Ber.*, 26, 2082—2083).—In a previous paper (this vol., i, 189), the author stated that the homologues of itaconic acid are scarcely altered by the action of boiling aqueous soda, only small quantities of readily soluble acids, which were taken for hydroxy-acids, being formed. Further investigation has, however, shown that these soluble acids are, in reality, new isomerides of the itaconic acids, and the name of *aticonic acids* has, therefore, been given to them. The new acids corresponding with dimethylitaconic, hexylitaconic, and phenylitaconic acids have all been prepared. They seem to bear the same relation to the itaconic acids that the citraconic acids do to the mesaconic acids. Thus, a solution of phenylitaconic acid in chloroform, on treatment with a few drops of a dilute solution of bromine in the same solvent, at once deposits crystals of pure phenylitaconic acid.

The aticonic acids differ from the itaconic and mesaconic acids by being readily soluble in water, whilst they are distinguished from the citraconic acids by not being volatile with steam; their barium and calcium salts are, moreover, much less soluble in water than those of the mesaconic acids. The melting points of the aticonic acids are higher than those of the citraconic, but lower than those of the itaconic and mesaconic acids, as is shown by the following table.

	Dimethyl.	Hexyl.	Phenyl.
Mesaconic acid ..	185—186°	153—154°	210°
Itaconic acid	162—163	129—130	180
Aticonic acid.	about 140°	about 110°	148
Citraconic acid ..	91—93°	86°	103—106°

On reduction with sodium amalgam, phenylaticonic acid is converted into the same benzylsuccinic acid as is given by the three other isomerides.

A. H.

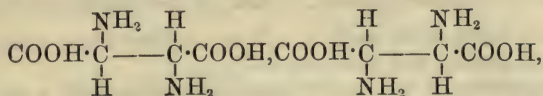
Isomeric Diamidosuccinic acids. By J. M. FARCHY and J. TAFEL (*Ber.*, 26, 1980—1990).—Tafel has shown (*Abstr.*, 1887, 468) that Lehrfeld's diamidosuccinic acid is obtained by the reduction of dihydroxytartaric osazone. On repeating the reduction experiment under the conditions described below, the authors isolated the diamidosuccinic acid previously described (*loc. cit.*), together with an isomeride; the experiments to be described show that the former is the meso-modification and the latter the racemic modification.

Dihydroxytartaric osazone (100 grams) is dissolved in a solution of sodium hydroxide (25 grams) in water (600 c.c.) at 0°, to which 1 kilo. of ice is added; 2½ per cent. sodium amalgam (3 kilos.) is then introduced in large portions at a time within five minutes, the mixture being agitated meanwhile and for half an hour subsequently, after which, 30 per cent. sulphuric acid (167 grams) is added slowly, the temperature rising to 40°. The mixture is shaken for an hour, cooled, and extracted with ether; the alkaline liquid is then acidified with dilute sulphuric acid, and the flocculent precipitate (16 grams) which separates, after 24 hours, is collected and washed with hot alcohol; it consists of crude mesodiamidosuccinic acid. The mother liquor is neutralised and shaken with ether, when, after several days, a crystalline precipitate (10 grams) of crude racemic diamidosuccinic acid separates.

$$\begin{array}{c} \text{NH}_2 \quad \text{NH}_2 \\ | \quad | \\ \text{COOH} \cdot \text{C} - \text{C} \cdot \text{COOH} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$$

Mesodiamidosuccinic acid, has been al-

ready described (*loc. cit.*). The copper salt is a blue precipitate containing 1 mol. H₂O; the diacetyl derivative, C₂H₂(NHAc)₂(COOH)₂, decomposes at 235°; and the dibenzoyl derivative melts at 213° with decomposition. If a neutral solution of the sodium salt, mixed with a dilute solution of sodium nitrite (2 mols.), is gradually added to dilute hydrochloric acid containing hydrogen chloride (5 mols.), meso-tartaric acid is formed; its isolation is described in detail.

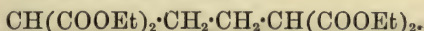
Racemic diamidosuccinic acid,

is purified by crystallising the crude acid from 2 per cent. hydrochloric acid; it crystallises in colourless prisms with H_2O , and exhibits the same general properties as the meso-modification, but differs from it in the following respects:—It is less soluble in hot water, and more soluble in dilute ammonia; when heated, it decomposes.

The *copper* salt forms deep blue, hydrated leaflets, and is insoluble in water; the *diacetyl* derivative decomposes at 235° , and the *dibenzoyl* derivative melts at 182° . The acid is converted into racemic acid when treated with dilute nitrous acid. A. R. L.

Anhydride Formation in the case of Substituted Succinic acids. By E. HJELT (*Ber.*, **26**, 1925—1928).—The acids were heated for a given time at a given temperature, and the amount of anhydride formed calculated from the observed loss of weight. The percentage of acid converted into anhydride increases in the following series, and, when the heating is continued for one hour at 160° , is expressed by the numbers in brackets: succinic acid, phenyl-, methyl- (14.1), ethyl- (14.5), propyl- (16.6), isopropyl- (29.6), and unsymmetrical dimethyl- (36.7) succinic acids, phthalic acid. The different radicles are found to exert here much the same influence as on the lactone formation in the case of γ -hydroxy-acids (*Abstr.*, 1891, 822). C. F. B.

Tetramethylene Derivatives. By W. H. PERKIN, JUN. (*Ber.*, **26**, 2243—2244; compare *Trans.*, 1887, 18).—The author has previously shown that ethylenic bromide reacts with ethylic sodiomalonate to form ethylic trimethylenedicarboxylate, together with about 3 per cent. of ethylic butanetetracarboxylate,



If, however, ethylenic chloride be substituted for the bromide, the yield of this second substance rises to about 30 per cent. The derivatives of this substance and of tetramethylenedicarboxylic acid, which can be easily prepared from it, are therefore being submitted to a renewed investigation.

Tetramethylenetetracarboxylic acid crystallises from water with $2\text{H}_2\text{O}$ in thick prisms, which melt at $198\text{--}203^\circ$, with decomposition into carbonic anhydride and tetramethylenedicarboxylic acid. The temperature of decomposition, which was formerly stated as $145\text{--}150^\circ$, is considerably lowered by small amounts of impurity.

Tetramethylenedicarboxylic acid melts at $137\text{--}138^\circ$ (formerly stated as 130°). The *dimethylic salt* boils at $222\text{--}223^\circ$. On boiling with acetic chloride, the acid is converted into the anhydride, $\text{C}_4\text{H}_6 \begin{smallmatrix} \text{CO} \\ > & & < \\ & \text{CO} \end{smallmatrix} \text{O}$ which melts at 75° and boils at $270\text{--}273^\circ$ without decomposition.

Tetramethylenedicarboxyanil, $C_4H_6<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>NPh$, is obtained by heating the anhydride with aniline. It crystallises from methyl alcohol in colourless plates, and melts at 127° .

The comparison of tetramethylenedicarboxylic acid with camphoric acid, which is now looked on by many chemists as isopropylmethyl-tetramethylenecarboxylic acid, $\begin{smallmatrix} CH_2 \cdot CMe \cdot COOH \\ | \\ CH_2 \cdot CPr^s \cdot COOH \end{smallmatrix}$, is also being prosecuted. On heating with sulphuric acid, the latter yields carbonic oxide and is converted into sulphocamphoric acid, whilst tetramethylenedicarboxylic acid is simply converted into the anhydride, no gas being evolved.

Many attempts have been made to ascertain whether tetramethylenedicarboxylic acid and the corresponding pentamethylenedicarboxylic acid, like the hexahydrophthalic acid to which they are closely allied in structure, occur in two isomeric forms (cis and trans), but hitherto with negative results.

Tetramethylenedicarboxylic anhydride is converted by the action of bromine and phosphorus into a substance which, when treated with water, yields *dibromotetramethylenedicarboxylic acid*, $\begin{smallmatrix} CH_2 \cdot CBr \cdot COOH \\ | \\ CH_2 \cdot CBr \cdot COOH \end{smallmatrix}$.

This acid crystallises from water in lustrous plates melting at $198-203^\circ$. On boiling with alkalis, it loses hydrogen bromide and forms an unsaturated acid, $\begin{smallmatrix} CH:CH \\ | \\ CH_2 \cdot CBr \cdot COOH \end{smallmatrix}$, which crystallises from

water in needles melting at 122° . The *barium salt* crystallises in plates, and, after drying in a vacuum, has the formula $(C_5H_4BrO_2)_2Ba$. When treated with bromine vapour, the acid takes up a molecule of bromine, forming the acid $C_5H_5Br_3O_2$, which is probably *tribromotetramethylenedicarboxylic acid*. The study of this substance is being continued in the hope of preparing from it the unsaturated acid, $\begin{smallmatrix} CH:CH \\ | \\ CH:C \cdot COOH \end{smallmatrix}$ the relation of which to benzene makes it a subject of great interest.

The details of these researches will be subsequently published.

A. H.

Synthesis of Pentamethylenecarboxylic acid. Hexamethylenecarboxylic (Hexahydrobenzoic) acid and Azelaic acid. By E. HAWORTH and W. H. PERKIN, Jun. (*Ber.*, 26, 2246—2250).—Pentamethylenic dibromide, prepared according to Gustavson and Demyanoff's method from pentamethylenediamine (*J. pr. Chem.*, [2], 39, 542), probably contains at least 60 per cent. of tetramethylenic dibromide.

By the action of ethylic sodiomalonate on this mixture of bromides, a product is obtained which can be separated by fractional distillation into two portions, one boiling at $240-250^\circ$ under 760 mm. pressure, and the other at $270-275^\circ$ under 50 mm. pressure. By hydrolysis of the first fraction, pentamethylenedicarboxylic acid is obtained, together with hexamethylenedicarboxylic acid.

Pentamethylenedicarboxylic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C}(\text{COOH})_2$, melts at 185° , is indifferent to soda at ordinary temperatures, and, on distillation, yields carbonic anhydride and *pentamethylenecarboxylic acid*, $\text{C}_5\text{H}_8\text{COOH}$. The latter is a colourless oil, boils at $214\text{--}215^\circ$, and is not oxidised by permanganate; it seems to be identical with Wislicenus and Gärtner's pentamethenecarboxylic acid (*Annalen*, 275, 339).

Hexahydrobenzoic (hexamethylenecarboxylic) acid is obtained by evaporating the mother liquors of the pentamethylenedicarboxylic acid on the water bath and distilling the residue. It is a colourless oil, boils at $231\text{--}233^\circ$, and solidifies when cooled.

The distillate mentioned above, as boiling at $270\text{--}275^\circ$ under 50 mm. pressure, consists of ethylic heptanetetracarboxylate, and when hydrolysed and heated at 220° , yields azelaic acid.

The authors failed to obtain heptane derivatives by the action of bromine on the disodium derivative of ethylic heptanetetracarboxylate. The product contained azelaic acid. E. C. R.

Acrylamide. By MOUREU (*Bull. Soc. Chim.*, [3], 9, 417—419).—Acrylamide is prepared by saturating a cooled benzene solution of acrylic chloride with dry ammonia. The solution, filtered from ammonium chloride and cooled, deposits thin, bright leaflets melting at $84\text{--}85^\circ$, and of a nacreous lustre in mass. Acrylamide is inodorous and easily soluble in water, alcohol, ether, chloroform, and most of the usual solvents. It melts sharply at $84\text{--}85^\circ$, gives off ammonia at 125° , and solidifies suddenly between 150° and 155° ; the product is almost of the same weight as the acrylamide taken. It is a tough, horny mass, non-crystalline, insoluble in all the usual neutral solvents, and has a bright, resinous fracture. Hydrochloric and acetic acids and alkaline solutions are without action on it, even after prolonged boiling. It appears to be a polymeride of very high molecular weight.

Acrylamide decomposes when heated above 155° : rapidly at $190\text{--}200^\circ$.

It readily forms an additive compound with bromine in the cold, small crystals of $\alpha\beta$ -dibromopropionamide being formed, soluble in chloroform, and melting at $130\text{--}133^\circ$. A small quantity of a more brominated derivative is formed at the same time, which cannot be entirely eliminated by crystallisation. W. T.

Substituted Acrylamides. By MOUREU (*Bull. Soc. Chim.*, [3], 9, 419—424).—The substances described do not polymerise, like acrylamide, when heated.

Methylacrylamide is a colourless liquid with a feeble odour of acetamide. It distils between 126° and 129° under a pressure of 30 mm., and under atmospheric pressure at 220° with partial decomposition. Its sp. gr., at 0° , is 1.018.

Ethylacrylamide closely resembles the methyl derivative, and distils at the same temperatures under similar conditions; sp. gr. = 0.978 at 0° .

Phenylacrylamide is obtained by the same process as the preceding compounds. It is a white, well-crystallised compound, soluble in boiling water, alcohol, and chloroform, but less soluble in benzene. It melts at 104–105°, begins to decompose at 275°, and the decomposition proceeds rapidly at 300°. No quinoline is produced even in presence of sulphuric acid, phosphoric anhydride, or zinc chloride.

Paratolylacrylamide forms fine, white, nacreous crystals melting at 141°.

Orthotolylacrylamide is a well crystallised substance melting at 109–110°.

Methylphenylacrylamide forms crystals melting at 76–77.5°.

Orthohydroxyphenylacrylamide melts at 123–124°. It is soluble in cold alkalis, hence the phenolic function is not affected during its formation.

W. T.

Preparation of Carbamide. By A. REYCHLER (*Bull. Soc. Chim.*, [3], 9, 427–429).—A dilute solution of sodium hypochlorite is gradually added to an aqueous solution of potassium cyanide; after the odour of cyanogen compounds has disappeared, an excess of ammonium sulphate is added, the whole heated to the boiling point, and then evaporated to dryness. The residue is extracted with 94 per cent. alcohol, and yields a crude product containing 89.4 per cent. of the theoretical quantity of carbamide.

If sodium peroxide is used as the oxidising agent, the yield is only 1.5 grams of carbamide from 10 grams of cyanide. Formamide yields 37.5 per cent. of the calculated amount of carbamide when oxidised by sodium hypochlorite in presence of sodium carbonate and treated as above; no carbamide is obtained, however, if sodium peroxide is substituted for hypochlorite.

W. T.

Action of Thionyl Chloride on Alkyl Carbamates. By G. SCHROETER and M. LEWINSKI (*Ber.*, 26, 2171–2174).—Thionyl chloride in benzene solution withdraws the elements of alcohol from 2 mols. of an alkyl carbamate, $\text{NH}_2\cdot\text{COOR}$, and an allophanate, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{COOR}$, is formed; other acid chlorides do not exercise this influence. This reaction was carried out in the cases $\text{R} = \text{Me}$, and $= \text{C}_5\text{H}_{11}$; the yield is a good one, respectively 70 and 50–55 per cent. of the theoretical, and the method is, consequently, well adapted for the preparation of allophanates. Contrary to expectation, cyanuric acid is not formed in the reaction; it is, however, if the substances are heated together in xylene solution at 150° in a sealed tube.

C. F. B.

Iodoso- and Iodoxy-derivatives of Benzene. By C. WILLGERODT (*Ber.*, 26, 1947–1950).—The *chloriodides* $\text{C}_6\text{H}_4\text{Cl}\cdot\text{ICl}_2$ [1 : 2, 1 : 3, and 1 : 4] and $\text{C}_6\text{H}_4\text{Br}\cdot\text{ICl}_2$ [1 : 3] were prepared by chlorinating the corresponding iodides; they are yellow, crystalline substances, and decompose respectively at 95–98°, 100°, 116–117°, and 104°. When treated with dilute aqueous soda, they yield the corresponding *iodoso-compounds* $\text{C}_6\text{H}_4\text{Cl}\cdot\text{IO}$, &c.; these are yellow, amorphous sub-

stances, and decompose at 85° , the first with explosion; when dissolved in acetic acid, they yield *acetyl derivatives*, $C_6H_4Cl \cdot I(OAc)_2$, &c., as colourless or white crystals melting respectively at 140° , 154 — 155° , 185 — 190° (with decomposition), and 163 — 164° . When the iodoso-compounds are heated on a watch-glass, or boiled with water, they decompose into iodides and *iodoxy-compounds*, $C_6H_4Cl \cdot IO_2$, &c.; these crystallise in white or colourless, hexagonal plates, and explode respectively at 203° , 233° , 243° , and 230° . C. F. B.

Action of Alkalis on Paranitrotoluene and on Paranitrotoluenesulphonic acid. By O. FISCHER and E. HEPP (*Ber.*, 26, 2231—2234).—Paranitrotoluene, when acted on by alkalis, yields a red, amorphous substance (Klinger, *Ber.*, 16, 941), which may perhaps be azoxystilbene (*Ber.*, 19, 3234). Paranitrotoluenesulphonic acid, in the same manner, yields the dyes "sun-yellow," "Mikado-brown," and "Mikado-orange." The authors have found that when paranitrotoluene is brought into a strong solution of caustic soda in methyl alcohol, and the mixture gently heated, an insoluble yellow mass is formed. This consists mainly of dinitrosostilbene, accompanied by smaller amounts of paradinitrodibenzyl and paradinitrostilbene, which may be extracted by alcohol and xylene respectively.

The *dinitrosostilbene*, $C_{14}H_{10}N_2O_2$, the constitution of which is not yet known, is insoluble in xylene, but may be recrystallised from ethylic benzoate or ethylic acetoacetate. It forms orange-yellow, round, crystalline nodules melting at 263° , and yields a cherry-red solution in concentrated sulphuric acid, but is insoluble in dilute acids or alkalis. On reduction, it is converted into paradiamidostilbene. When paranitrotoluene is treated with a less concentrated solution of caustic soda, the red, amorphous substance already referred to is obtained, and it is also formed when dinitrodibenzyl is submitted to the same treatment.

Paranitrotoluenesulphonic acid is converted, by the action of concentrated aqueous soda, into *disodium dinitrosostilbenedisulphonate*; it separates from alcohol in compact, reddish crystals, and gives with barium chloride an orange-yellow precipitate of the corresponding *barium* salt. Dinitrosostilbenedisulphonic acid is converted by oxidation into dinitrostilbenedisulphonic acid, and by energetic reduction into diamidostilbenedisulphonic acid. Moderate reduction, on the other hand, yields colouring matters of redder shade, which are probably azoxy- and azo-derivatives. When paranitrotoluenesulphonic acid is treated with more dilute aqueous soda, the colouring matters known as "sun-yellows" are formed, and these do not yield dinitrosostilbenedisulphonic acid on recrystallisation. A. H.

Synthesis of Phenols from Ethylic Acetoacetate. By E. KNOEVENAGEL (*Ber.*, 26, 1951—1952).—By the condensation of ethylic acetoacetate with aldehydes, substances were obtained (this vol., i, 419) which are derivatives of (1) (see next page); these form dibromo-additive compounds, which, when heated on the water bath, lose hydrogen bromide and yield phenols:



In this way, 3-methyl- Δ_2 -ketohehexene yields 1 : 3-cresol, and 3 : 5-dimethyl- Δ_2 -ketohehexene yields 1 : 3 : 5-xyleneol.

C. F. B.

Action of Chlorine on Catechol and Orthamidphenol. By T. ZINCKE and F. KÜSTER (*Ber.*, 26, 2104—2117; compare Abstr., 1890, 1255).—By the action of alkalis on $\gamma\gamma$ -hexachloroketopentene (m. p. 92°) at 40—50°, a bibasic acid, $\text{C}_5\text{Cl}_4\text{H}_2\text{O}_4$, is formed, and is being further investigated. It has already been shown (Abstr., 1890, 754) that, on treating the ketone with alkali at 0°, an unstable acid is formed which is isomeric with that (m. p. 127°) from the $\beta\gamma$ -ketone; it appears to be pentachlorobutenecarboxylic acid $\text{CCl}_2\text{:C}\cdot\text{CCl}\cdot\text{CCl}_2\cdot\text{COOH}$, crystallises from light petroleum, and melts at 97—98°. The acid is soluble in water at ordinary temperatures; on warming, a turbidity is produced, and carbonic anhydride evolved (see below). The sodium salt, $\text{C}_4\text{Cl}_5\cdot\text{COONa}$, crystallises in silvery, lustrous plates. The $\gamma\gamma$ -ketone, $\text{C}_5\text{Cl}_5\text{BrO}$, is decomposed by the action of soda at 0° in a similar manner to the pentachloro-ketone, and yields a corresponding acid, $\text{C}_4\text{Cl}_4\text{Br}\cdot\text{COOH}$, which is deposited in microscopic prisms; it melts at 100—100·5°, resolidifies, and melts again at 114°; on crystallisation from light petroleum, long, colourless needles are obtained; from ether and light petroleum, compact, granular crystals; both forms melt at 110°. On heating with water, it undergoes a similar decomposition to the pentachloro-acid, but the product, which is an oil, volatile with steam, has not been isolated. *Pentachlorobutidene* (or *-butine*), $\text{C}_4\text{Cl}_5\text{H}$, is prepared by boiling the pentachloro-acid with water; on distilling the product with steam, it passes over as a colourless oil with a characteristic, penetrating odour, and boils at 125° under 75—80 mm. pressure. The compound is extremely stable, and does not combine with bromine; attempts to eliminate hydrogen chloride were unsuccessful; it may be represented by the formula $\text{CCl}_2\text{:C}\cdot\text{CCl}\cdot\text{CHCl}_2$ or $\text{CCl}_2\text{:C}\cdot\text{C}\cdot\text{CHCl}_2$. In addition to the preceding substance, a solid was obtained by the decomposition of the acid; it is not volatile with steam, and has not been investigated.

It has already been shown that, on reduction, the above pentachloro-acid yields an acid of the formula $\text{C}_5\text{H}_5\text{O}_2$; with proper precautions, which are fully described in the paper, the yield is 30—35 per cent. of the theoretical; the same compound is obtained from the bromo-acid $\text{C}_4\text{Cl}_4\text{Br}\cdot\text{COOH}$, and also from that derived from the $\beta\gamma$ -ketone (m. p. 32°); the fact that this acid readily combines with hydrogen bromide, and that the product only yields traces of valerolactone, caused it to be regarded as propylideneacetic acid; Vieffhaus has recently shown (this vol., i, 392) that the compound, termed by Ott propylideneacetic acid, contained ethylidene-propionic acid, and, on comparison, it is found that the above acid, $\text{C}_4\text{H}_7\cdot\text{COOH}$, and ethylidenepropionic acid yield identical salts and oxidation products. This conclusion is not in harmony with the observations of Fittig and Fränkel, who state that ethylidenepropi-

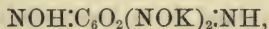
onic acid is readily converted into valerolactone (*Annalen*, **255**, 27). The barium salt, insoluble in alcohol, described by Ott (*Abstr.*, 1891, 1453) as dissolving more readily in cold water than in hot, crystallises from hot water on cooling the solution. J. B. T.

Dinitrocatechol and its Conversion into Nitranilic acid. By R. NIETZKI and F. MOLL (*Ber.*, **26**, 2182—2184).—When diacetyl-catechol is dissolved in pure nitric acid at 0°, a *dinitro-derivative* is obtained in yellow needles melting at 124°; this, on hydrolysis, yields *dinitrocatechol* [(OH)₂:(NO₂)₂ = 1:2:3:5 probably], crystallising in yellow needles, and melting at 164°. When this is dissolved in a mixture of nitric and sulphuric acids, it is converted into nitranilic acid, and this is shown to be identical with the “dinitrodioxy-quinone” obtained by Gruber (*Abstr.*, 1879, 644) by the action of nitrous acid on protocatechuic acid; Gruber’s compound is not, therefore, a chemical individual. Dinitrocatechol, or, better, its diacetyl derivative, when reduced with stannous chloride, yields *diamidocatechol*; the *hydrochloride*, with 2HCl, was prepared; the free base oxidises rapidly in the air with formation of steel-blue needles of a compound C₆H₂(NH)₂(OH)₂. The base does not react with orthodiketones, and is consequently not an orthodiamine.

C. F. B.

Derivatives of Phloroglucinol. By R. NIETZKI and F. MOLL (*Ber.*, **26**, 2185—2187).—Pure nitric acid at 0° converts triacetyl-phloroglucinol into a nitro-derivative, which, when treated with potash, yields the potassium salt of trinitrophloroglucinol. This, when reduced with stannous chloride, yields *triamidophloroglucinol*, the *hydrochloride* of which, with 2HCl, forms colourless needles turning brown in the air. The base itself is oxidised by manganese dioxide in alkaline solution to croconic acid.

When the potassium salt of triuitrosophloroglucinol is heated at 100° with aqueous ammonia in a sealed tube, a compound,



is formed; if the phenol is itself used, instead of its potassium salt, the product has the composition C₆O(NO₂)₃(NH)₂ + NH₃.

C. F. B.

Parachlororthotoluidine. By A. CLAUS (*Annalen*, **276**, 347—349).—Claus and Stapelberg have stated (this vol., i, 580) that parachlororthotoluidine melts at 16°; the author finds that when the base having the last-mentioned melting point is thrice rapidly distilled over a free flame, a white, crystalline preparation is obtained; this, when crystallised from alcohol, melts at 29—30°, which value agrees with that obtained by other observers.

A. R. L.

Action of Ethylenediamine on Nitrophenols, their Ethers and corresponding Halogen Derivatives. By K. JEDLIČKA (*J. pr. Chem.*, [2], **48**, 193—208).—Orthonitrophenol and ethylenediamine, when heated together in a sealed tube at 180—190° for 10 hours,

yield tarry products, from which no definite compound can be isolated. When heated at 170° , scarcely any action takes place.

Diorthonitrodiphenylethylenediamine, $C_6H_4(NH \cdot C_6H_4 \cdot NO_2)_2$, is obtained by heating orthonitranisole with ethylenediamine at 180° in a sealed tube. The yield is 20 per cent. on the weight of the nitranisole. A yield of 16 per cent. is obtained by heating orthobromonitrobenzene with ethylenediamine at 120 – 130° . *Diorthonitrodiphenylethylenediamine* crystallises from benzene in small, interlacing, orange-red needles, melts at 190° , and decomposes at a higher temperature. It is a weak base, dissolves in concentrated mineral acids, and is precipitated in orange-yellow flocks on the addition of water. The *diacetyl derivative* crystallises in small, transparent, pale yellow prisms, and melts at 215 – 216° . The *dibenzoyl derivative* separates from solution in oily drops which solidify after a time, and then melts at 218 – 220° .

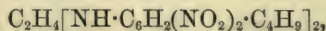
Diorthonitrodiphenylethylenediamine cannot be obtained by heating a mixture of orthonitraniline and ethylenic bromide. At 150° , scarcely any action takes place, and at higher temperatures dark, uninviting products are obtained.

A yield of 40–50 per cent. of orthobromonitrobenzene is obtained when bromobenzene is treated with concentrated nitric acid at a temperature not exceeding -10° . At -40 – -50° no action takes place.

Diparanitrodiphenylethylenediamine is obtained in small quantities by heating paranitrophenol and ethylenediamine for some hours at 160 – 170° , and then for six hours at 190 – 200° . A 14 per cent. yield is obtained by heating paranitranisole with ethylenediamine at 160 – 170° ; and a 30 per cent. yield is obtained in a similar way from parabromonitrobenzene at 130° . It crystallises from nitrobenzene in yellowish-brown microscopic needles, melts at 216° , has no basic properties, but dissolves in concentrated mineral acids, and is reprecipitated by the addition of water.

Tetranitrodiphenylethylenediamine cannot be prepared from orthoparadinitrophenol and ethylenediamine. A yield of 25 per cent. is obtained when methoxydinitrobenzene is employed, and an almost theoretical yield is obtained from bromodinitrobenzene. It crystallises in small, yellow, angular aggregates, melts at 302 – 303° , and is indifferent to alkalis and acids.

Tetranitroditertiarybutyldiphenylethylenediamine,⁷



cannot be obtained from dinitrotertiarybutylphenol (m. p. 93°). A yield of 50–60 per cent. is, however, obtained from methoxydinitrobutylbenzene (m. p. 102°) by heating on the water bath or in a sealed tube at 120 – 130° for three hours. It crystallises in beautiful, small, sulphur-yellow needles, melts at 174 – 175° , and has no basic properties.

Hexanitrodiphenylethylenediamine cannot be obtained from picric acid. A yield of 70 per cent. is obtained by adding ethylenediamine to an alcoholic solution of methylic picrate, and warming the mixture on the water bath. It is also easily obtained by adding ethylenediamine to an alcoholic solution of picryl chloride, when much heat is

developed. It crystallises from nitrobenzene in beautiful, small, lemon-yellow leaflets, melts at 230° , decomposes at a higher temperature, and gives brownish-red solutions in aqueous alkalis. When heated with aqueous alkalis, it yields ethylenediamine and alkali picrate. It dissolves in concentrated sulphuric acid in the cold, and is precipitated by water in pale yellow flocks. When heated with sulphuric acid, it yields picric acid. E. C. R.

Molecular Weight of the Carbodiimides. By C. SCHALL (*Zeit. physikal. Chem.*, **12**, 145—154).—Four modifications of carbophenydiimide which the author has investigated give numbers for the elevation of the boiling point of acetone and ethylic acetate which correspond with the normal molecule $C(NC_6H_5)_2$. The numbers obtained from the depression of the freezing point of benzene indicate double and even triple molecules. The molecular weight of the carbodiparatolylimides was found to be always somewhat higher than that corresponding with the formula $C(NC_7H_7)_2$. J. W.

Introduction of the Phenyl Group into Cycloïd Compounds. By R. MÖHLAU and R. BERGER (*Ber.*, **26**, 1994—2004).—Diazobenzene chloride reacts with benzene in presence of synthetic aluminium chloride (this vol., i, 161), forming chlorobenzene and diphenyl. When diazobenzene chloride is mixed with a little toluene, and a mixture of warm toluene and aluminium chloride gradually added with shaking, the whole being finally heated to boiling, chlorobenzene and a mixture consisting of para- and perhaps ortho-methylphenylbenzene are obtained. The diazochlorides of ortho- and para-toluene, on treatment with either benzene or toluene, yield the corresponding chlorotoluenes. Diazobenzene chloride and diphenyl, in presence of aluminium chloride, yield chlorobenzene, paradiphenylbenzene (m. p. 204°), and isodiphenylbenzene (Schulze, *Annalen*, **174**, 233; **203**, 129).

For the action of diazobenzene chloride on naphthalene see this vol., i, 522.

β -Diazonaphthalene chloride and benzene react in presence of aluminium chloride, forming β -chloronaphthalene (m. p. 57 — 58°). A phenylthiophen is obtained by the action of diazobenzene chloride on thiophen in presence of aluminium chloride; it forms silvery leaflets, melts at 56 — 57° , and boils at 254° . It thus differs from α -phenylthiophen (Kues and Paal, *Abstr.*, 1887, 238), and is probably the β -modification. Diazobenzene chloride reacts very energetically with pyridine, forming a mixture of 1-phenylpyridine and 3-phenylpyridine; it also reacts with equal energy with quinoline, forming 1-phenylquinoline. A. R. L.

Reaction of Hydrazine Hydrate with the Nitro-, Nitroso-, and Isonitroso-groups. By R. v. ROTHENBURG (*Ber.*, **26**, 2060—2061).—The preliminary experiments of the author show that the isonitroso-group (acetoxime, benzaldoxime) is removed by the action of an excess of hydrazine hydrate and replaced by the hydrazo-group (NH_2N) . The nitroso- and nitro-groups, on the other hand (nitro-

benzene, paranitrosodimethylaniline, diphenylnitrosamine), are reduced to the amido-group.
A. H.

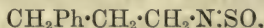
Thionylbenzylhydroxylamine and Dibenzoxycarbamide. By A. MICHAELIS and G. SCHRÖTER (*Ber.*, 26, 2155—2157.)—When an ethereal solution of thionyl chloride is added drop by drop to an ethereal solution of α -benzylhydroxylamine, the hydrochloride of the latter separates, and *thionylbenzylhydroxylamine*, $\text{OBz}\cdot\text{N}\cdot\text{SO}$, remains in the solution, and may be purified, after the ether has been driven off, by distillation under reduced pressure. It is a yellowish liquid, boiling at $153\text{--}154^\circ$ under 50 mm. pressure, is decomposed by soda into sulphurous anhydride and benzylhydroxylamine, yields thionylphenylhydrazone, $\text{NHPh}\cdot\text{N}\cdot\text{SO}_2$, with phenylhydrazine acetate, and in the presence of moisture forms *benzylhydroxylamine benzylthiohydroxylamate*, $\text{OBz}\cdot\text{NH}\cdot\text{SO}_2\cdot\text{NH}_3\cdot\text{OBz}$, which crystallises in white plates, melts with decomposition at $84\text{--}85^\circ$, and with benzaldehyde yields sulphurous anhydride and α -benzylbenzaldoxime.

When a toluene solution of carbonyl chloride is added to a benzene solution of α -benzylhydroxylamine, *dibenzoxycarbamide*, $\text{CO}(\text{NH}\cdot\text{OBz})_2$, is formed; it crystallises in minute needles which melt at 88° .

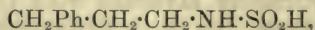
C. F. B.

Thionylamines of Unsaturated Bases. Thionylphenylpropylamine. By A. MICHAELIS and W. JACOB (*Ber.*, 26, 2158—2162).—Allylamine does not yield a thionylamine with thionyl chloride, but butenylmethylmethylaniline (butallylmethylcarbinamine), in which the double bond is farther removed from the amido-group, does yield *methylbutenylmethylthionylamine* (butallylmethylcarbinthionylamine), $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{N}\cdot\text{SO}$, when treated in ethereal solution with thionyl chloride. This thionylamine is a colourless liquid which boils at $156\text{--}158^\circ$, and has sp. gr. 0.9986 at 15° ; it is decomposed by alkalis.

Phenylpropylamine, prepared by reducing the phenylhydrazone of cinnamaldehyde (compare Tafel, *Abstr.*, 1886, 940), is a colourless liquid which boils at $216\text{--}218^\circ$, and has sp. gr. = 0.951 at 15° ; it forms a pale-yellow *platinochloride*, $2\text{C}_9\text{H}_{13}\text{N}\cdot\text{H}_2\text{PtCl}_6$, which melts with decomposition at 233° ; and, with phenylthiocarbimide, it yields *phenylpropylphenylthiocarbamide*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, melting at $95\text{--}96^\circ$. When its hydrochloride is heated with a benzene solution of thionyl chloride, *phenylpropylthionylamine*,



is formed; this is a brownish-yellow liquid, which is decomposed by alkalis or on heating. With sulphurous acid in ethereal solution, phenylpropylamine yields *phenylpropylthionamic acid*,



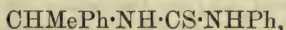
a white, amorphous powder, which with phenylpropylamine yields lustrous crystals of *phenylpropylamine phenylpropylthionamate*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{SO}_2\cdot\text{NH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, decomposing at 290° , and with benzaldehyde quadratic plates of *benzaldehyde phenyl-*

propylthionamate, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{SO}_2\text{H})\cdot\text{CHPh}\cdot\text{OH}$, melting at $105\text{--}106^\circ$.
C. F. B.

Action of Thionyl Chloride on Benzylamine and its Homologues; some Derivatives of the latter. By A. MICHAELIS, G. SCHRÖTER, and E. LINOW (*Ber.*, **26**, 2162—2171).—The action of thionylaniline on benzylamine (compare this vol., i, 515) gives rise to benzylideneaniline, free sulphur, probably ammonia, and, in addition, ammonium thiosulphamate and trithionamate; these last two substances dissolve in water, yielding respectively ammonium thiosulphate and trithionate. *Ammonium trithionate* has not hitherto been prepared; it forms anhydrous prismatic crystals.

The action of thionyl chloride on the homologues of benzylamine was also studied. With the tolylmethylamines, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{NH}_2$, it forms thionyltolylmethylamines, which yield aldehydes when heated. With derivatives of the type $\text{Ph}\cdot[\text{CH}_2]_n\cdot\text{NH}_2$ [$n > 1$], thionylamines are formed, which yield no aldehydes. With derivatives of the type $\text{CHPh}\cdot\text{NH}_2$ [$\text{R} = \text{Me}$ or Ph], thionylamines are formed which, at a comparatively high temperature, yield ketones. Thiocarbamides were prepared from the amines by the addition of carbon bisulphide; whilst the action of sulphurous anhydride on the amines gave rise to thionamic acids, the amine salts and benzylidene derivatives of which were also prepared. The thionyltolylmethylamines, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{N}:\text{SO}$ [1 : 2, 1 : 3, and 1 : 4], are light-brown liquids, which yield aldehydes when heated.

Thionyl-β-phenylethylamine, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{N}:\text{SO}$, is a yellow liquid, boiling at $170\text{--}173^\circ$ under 25 mm. pressure; *β-phenylethylthionamic acid*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{SO}_2\text{H}$, is a white, amorphous powder, which sublimes without melting, and yields a *β-phenylethylamine salt*, crystallising in rhombic prisms, which also sublime without melting, and a *benzaldehyde derivative*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{N}(\text{SO}_2\text{H})\cdot\text{CHPh}\cdot\text{OH}$, in white crystals melting at 114° ; *acetyl-* and *benzoyl-β-phenylethylamine*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NHBz}$, melt at 51° and 116° respectively; *phenyl-β-phenylethylcarbamide*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, melts at 106° ; the *picrate* of *β-phenylethylamine* at 168° . *Thionyl-α-phenylethylamine*, $\text{CHMePh}\cdot\text{N}:\text{SO}$, is a brownish-yellow liquid, and yields acetophenone when heated; *α-phenylethylthionamic acid*, $\text{CHMePh}\cdot\text{NH}\cdot\text{SO}_2\text{H}$, resembles the corresponding *β-compound*, but does not yield a benzaldehyde derivative; *phenyl-α-phenylethylcarbamide*,

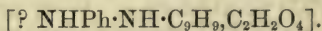


forms silky crystals melting at 106° ; *di-α-phenylethylthiocarbamide*, $\text{CS}(\text{NH}\cdot\text{CHMePh})_2$, melts at 163° ; *α-phenylethylamine α-phenylethylthiocarbamate* melts at 143° ; the *picrate* at 189° .

Thionylbenzhydrylamine, $\text{CHPh}_2\cdot\text{N}:\text{SO}$, is a light yellow liquid, which boils at 88° under 35 mm. pressure, and yields benzophenone when heated under atmospheric pressure; *benzhydrylamine sulphate* melts at 244° ; the *acetate* at 141° ; with benzaldehyde, the amine yields a *benzylidene* compound, $\text{CHPh}_2\cdot\text{N}:\text{CHPh}$, melting at $98\text{--}99^\circ$, and in a similar way *orthohydroxybenzylidene*, $\text{CHPh}_2\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, *methoxybenzylidene*, $\text{CHPh}_2\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, and *cinnamylidene*,

$\text{CHPh}_2\cdot\text{N}\cdot\text{CH}\cdot\text{CHPh}$, compounds, melting at 131° , 110 — 111° , and 128° , were prepared from salicylic, anisic, and cinnamic aldehydes; the last named yields a *dibromide* which decomposes at 170 — 180° ; *phenylbenzhydrylaminethiocarbamide*, $\text{CHPh}_2\cdot\text{NH}\cdot\text{CS}\cdot\text{NPh}$, melts at 180.5° .
C. F. B.

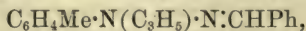
Derivatives of Unsymmetrical Allylphenylhydrazine and Allyltolylhydrazine. By A. MICHAELIS and K. LUXEMBOURG (*Ber.*, 26, 2174—2181).—It was left doubtful whether the compound obtained by the action of mercuric oxide on unsymmetrical allylphenylhydrazine (Abstr., 1889, 1161) is an azo-compound, $\text{NPh}\cdot\text{NC}_3\text{H}_5$, or a pyrazole derivative. The former hypothesis is the more probable, for the corresponding cinnamyl compound yields aniline when reduced with zinc and acetic acid; when reduced with sodium amalgam in alcoholic solution, it yields a base, the formula for the oxalate of which is given as $\text{C}_6\text{H}_5\text{NC}_9\text{H}_9\text{NH}_2\cdot\text{C}_2\text{H}_2\text{O}_4$



Thionylallylphenylhydrazone, $\text{C}_3\text{H}_5\cdot\text{NPh}\cdot\text{N}\cdot\text{SO}$, obtained by shaking an acetic acid solution of allylphenylhydrazine with thionylaniline, is a pale yellow oil decomposed by alkalis. When allylphenylhydrazine, $\text{C}_3\text{H}_5\cdot\text{NPh}\cdot\text{NH}_2$, is treated with pyruvic acid, the *hydrazone*, $\text{C}_3\text{H}_5\cdot\text{NPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{COOH}$, separates as a reddish oil, which is converted into *allylindolecarboxylic acid*, $\text{C}_6\text{H}_4\langle\text{---}\frac{\text{N}(\text{C}_3\text{H}_5)}{\text{CH}}\text{---}\rangle\text{C}\cdot\text{COOH}$, when heated with hydrochloric acid on the water bath. This acid forms white needles which melt at 182° (after sublimation, at 177°); the *barium salt*, with $2\text{H}_2\text{O}$, crystallises in reddish plates. When heated at 200° , best in a sealed tube, it loses carbonic anhydride, and yields *allylindole*, a colourless liquid which boils at 252° , and will absorb bromine.

Allylphenylhydrazine condenses with ethylic acetoacetate in the presence of zinc chloride to form *ethylic allylmethylindolecarboxylate*, $\text{C}_6\text{H}_4\langle\text{---}\frac{\text{N}(\text{C}_3\text{H}_5)}{\text{C}(\text{COOEt})}\text{---}\rangle\text{CMe}$; it crystallises in small plates. The yield is poor. The *acid* itself forms white needles, and melts at 167 — 168° ; when heated to 180° it evolves carbonic anhydride, and yields *allylmethylindole*, a pale yellow oil of high-boiling point.

Allylparatolylhydrazine, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}(\text{C}_3\text{H}_5)\cdot\text{NH}_2$, was prepared from paratolylhydrazine and allylic bromide; it is a pale yellow oil, which boils at 160 — 170° under 90 mm. pressure, and rapidly darkens when exposed to the air; the *hydrochloride*, with HCl , forms white plates which melt at 129° , and very quickly redden in the air. With benzoic and cinnamic aldehydes, the hydrazine yields respectively *benzylidene-* and *cinnamylidene-allylparatolylhydrazine*,

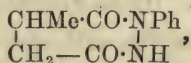


&c., the former as white needles melting at 61° , the latter as yellow needles melting at 118° . By ferric chloride, it is oxidised to *diallyl-diparatolyltetrazone*, $\text{N}_2[\text{N}(\text{C}_3\text{H}_5)\cdot\text{C}_6\text{H}_4\text{Me}]_2$, which crystallises in plates and melts at 104° ; by mercuric oxide, it is oxidised to *azoallyltolyl*,

$\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{N}\cdot\text{C}_3\text{H}_5$, which is a white, crystalline substance melting at $96-97^\circ$, and distilling at 110° under 20—30 mm. pressure.

C. F. B.

Action of Chlorides of Bibasic acids on Hydrazines. By A. MICHAELIS (*Ber.*, 26, 2181—2182; compare this vol., i, 370).—Phenylhydrazine hydrochloride, suspended in benzene, and treated with pyrotartaric chloride, yields *phenylmethylorthopiperazone*,



melting at 204° , the *acetyl derivative* of which melts at 174° ; with phthalic chloride, it yields β -phthalylphenylhydrazine. With dibromosuccinic chloride, paratolylhydrazine yields a compound

$\text{CH}\cdot\text{CO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$
 $\text{CH}\cdot\text{CO}\cdot\text{NH}$; with succinic chloride itself, *tolylorthopiperazone*

$\text{CH}_2\cdot\text{CO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$
 $\text{CH}_2\cdot\text{CO}\cdot\text{NH}$, is formed. Fumaric chloride does not react with

these hydrazines. With acetylphenylhydrazine, succinic chloride yields *acetyl- α -succinylphenylhydrazine*, $\text{C}_2\text{H}_4(\text{CO}\cdot\text{NPh}\cdot\text{NHAc})_2$; a similar compound was obtained from acetyltolylhydrazine, and also from fumarylphenyl- and fumaryltolylhydrazine.

C. F. B.

Bromination of Aromatic Hydrazines and Amines. By L. MICHAELIS (*Ber.*, 26, 2190—2197).—When bromine is allowed to act on aromatic amines and hydrazines in the presence of strong hydrochloric acid, it enters the benzene ring, preferably in the para-position to the nitrogen atom. In the case of the hydrazines, it also acts as an oxidising agent, converting the brominated derivatives into diazo-compounds; for example, phenylhydrazine yields bromodiazobenzene, in addition to bromophenylhydrazine; and this reaction becomes the chief one, if the above-mentioned para-position is already occupied. The bromination is carried out at 0° , and in the presence of a large excess of concentrated hydrochloric acid. The melting points given are mostly uncorrected.

Phenylhydrazine yields parabromophenylhydrazine, the *acetyl derivative* of which forms colourless prisms melting at 167° , and parabromodiazobenzene. Acetylphenylhydrazine yields acetyldibromophenylhydrazine [$\text{N}_2\text{H}_2\text{Ac} : \text{Br}_2 = 1 : 2 : 4$], together with dibromophenylhydrazine and dibromodiazobenzene. Orthotolylhydrazine yields parabromorthotolylhydrazine [$\text{Me} : \text{N}_2\text{H}_3 : \text{Br} = 1 : 2 : 5$], forming prisms melting at 104° ; the *hydrochloride* melts at 183.5° , the *acetate* at 172° with decomposition. It also yields bromorthodiazotoluene, the *perbromide* of which, $\text{C}_6\text{H}_3\text{MeBr}\cdot\text{N}_2\text{Br}_3$, forms yellowish-red needles, and is converted by ammonia into the *diazoimide*, $\text{C}_6\text{H}_3\text{MeBr}\cdot\text{N}_3$, which was obtained crystallised. Paratolylhydrazine yields some *bromoparatolylhydrazine*, crystallising in needles melting at $94.5-95^\circ$, together with much *bromoparadiazotoluene*, the *perbromide* of which is an explosive substance and yields a *diazoimide*, which was obtained crystallised. β -Naphthylhydrazine yields nothing but *bromodiazonaphthalene*, the *perbromide* of which is an explosive, yellow, crystalline

substance, and yields a *diazoimide*, forming colourless needles, and melting at 111° . α -Naphthylamine yields *bromo- α -naphthylamine*, which crystallises in small, white needles, and melts at 118.5° ; the *hydrochloride* forms white prisms, which decompose above 200° . β -Naphthylamine yields dibromo- β -naphthylamine [$\text{NH}_2 : \text{Br}_2 = 2 : 1 : 3'$].
C. F. B.

Benzylbenzaldoxime. By E. BECKMANN (*Ber.*, 26, 2272—2285; Abstr., 1891, 194).—Benzylbenzaldoxime, $\text{O} < \begin{smallmatrix} \text{CHPh} \\ | \\ \text{N} \cdot \text{C}_7\text{H}_7 \end{smallmatrix}$, when dis-

solved in benzene and treated with benzoic chloride, gives a precipitate of benzylbenzaldoxime hydrochloride which, after a time, dissolves, and the mixture then deposits benzylbenzamide, $\text{NH} \cdot \text{Bz} \cdot \text{C}_7\text{H}_7$. 0.045 gram of benzoic chloride is sufficient to convert 1 gram of the benzaldoxime into benzylbenzamide. In ethereal solution, a small quantity of benzylbenzamide is obtained, and then a separation of beautiful lustrous needles takes place, which contain benzylbenzamide and benzylbenzaldoxime in molecular proportion. If benzylbenzaldoxime is treated with benzoic chloride at low temperatures without any solvent, benzylbenzamine is obtained, and at the boiling temperature a mixture of benzylbenzamide and benzoylbenzylbenzamide. Benzoic anhydride has no action on benzylbenzaldoxime at low temperatures; at 120 — 180° , however, benzoylbenzylbenzamide is formed.

Benzoylbenzylbenzamide, $\text{NBz}_2 \cdot \text{C}_7\text{H}_7$, melts at 107 — 108° ; when heated at higher temperature, it yields a deep blue liquid which gives a blue solution in alcohol, turns green when treated with acids, and is decolorised by reducing agents. It is not altered by aqueous potassium hydroxide, boiling acetic acid, or acetic anhydride, and when boiled with benzoic anhydride is converted into benzoylbenzamide.

Acetic chloride and acetic anhydride act on benzylbenzaldoxime in a similar way to benzoic chloride and anhydride respectively. *Acetylbenzylbenzamide*, $\text{NAcBz} \cdot \text{C}_7\text{H}_7$, was obtained as an oil which was not pure. When heated at high temperatures, it yields a blue compound, and when treated with sodium and alcohol is converted into benzylbenzamide.

Phosphoric chloride and phosphorus anhydride, used in relatively small quantities, convert benzylbenzaldoxime into benzylbenzamide, in a similar way to the above acid chlorides. A mixture of acetic acid, acetic anhydride, and hydrogen chloride behaves similarly. Hydrochloric acid, acetic acid, and alcohol are without action on benzylbenzaldoxime.

α -Benzoyl- β -benzylhydroxylamine, $\text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{O} \cdot \text{COPh}$, is obtained by shaking the aldoxime with ether and benzoic chloride, and after separating the precipitate of benzylbenzaldoxime hydrochloride, allowing the solution to evaporate by exposure to air. The product it then treated with soda, when the hydroxylamine derivative is obtained as an oil; if treated with sodium and alcohol, it yields ethylic benzoate and benzoic acid. When subjected to steam distillation in the presence of alkali, or when heated with hydrochloric acid, β -benzoylhydroxylamine is obtained. The *benzoyl derivative*, $\text{C}_7\text{H}_7 \cdot \text{NBz} \cdot \text{O} \cdot \text{COPh}$, is obtained by boiling it with benzoic chloride.

It crystallises in tablets, melts at 96—97°, and, when treated with sodium and alcohol, yields ethylic benzoate and β -benzoyl- β -benzylhydroxylamine; the latter crystallises in white needles and melts at 106°.

α -Acetyl- β -benzylhydroxylamine, $C_7H_7 \cdot NH \cdot OAc$, is obtained in a similar way to the preceding compound; it is an oil. The *hydrochloride* melts at 105—110°. When boiled with acetic chloride, the oily *diacetyl compound*, $C_7H_7 \cdot NAc \cdot OAc$, is obtained; the latter, when treated with sodium and alcohol, yields the compound $C_7H_7 \cdot NAc \cdot OH$, which crystallises in tablets, and melts at 124°.

E. C. R.

Action of Isocyanates on Aromatic Aldoximes. By H. GOLDSCHMIDT and W. H. VAN RIETSCHOTEN (*Ber.*, 26, 2087—2100).—Carbanilidoparamethoxybenzosynaldoxime (m. p. 80°) has previously been described (Abstr., 1890, 1261); on recrystallisation from warm ether, an isomeric compound is formed in aggregates of colourless needles; this melts at 82° with evolution of gas, and on treatment with soda yields methoxybenzonitrile, together with very small quantities of diphenylcarbamide and regenerated aldoxime. Carbanilidoparamethoxybenzantialdoxime could only be obtained in one modification melting at 103°, instead of 82° as previously stated. *Carborthotoluidoparamethoxybenzosynaldoxime*, $OMe \cdot C_6H_4 \cdot \overset{\text{CH}}{\underset{\text{N} \cdot O \cdot CO \cdot NH \cdot C_6H_4 \cdot Me}{\parallel}} \cdot$ is formed

from orthotolylic isocyanate and the synaldoxime, at ordinary temperatures, and crystallises in greenish, flat prisms melting at 81° with decomposition. On warming with ether, a second modification is obtained in colourless, dendritic needles melting at 98°. *Carborthotoluidoparamethoxybenzantialdoxime*, $OMe \cdot C_6H_4 \cdot \overset{\text{CH}}{\underset{C_6H_4 \cdot Me \cdot NH \cdot CO \cdot NO}{\parallel}} \cdot$ only exists

in one form, crystallising in clusters of colourless needles which melt at 127°. *Carboparatoluidoparamethoxybenzosynaldoxime* is prepared by the action of paratolylic isocyanate on either the “syn-” or “anti-” aldoxime, and is deposited in pale yellow prisms which become colourless on heating to 70—80°, and melt at 106° with evolution of gas. On treatment with soda, it is resolved into paraditolylcarbamide, paratoluidine, paramethoxybenzonitrile, and, in relatively large quantity, regenerated synaldoxime. The isomeric compound is formed by boiling with ether, and crystallises in long, slender needles melting at 106° with decomposition. By the action of soda, it yields the same products as the yellow substance; the amount of aldoxime is, however, small, that of nitrile large. *Carboparatoluidoparamethoxybenzantialdoxime* is obtained from the mother liquor after the removal of the yellow “syn-” derivative, but the most favourable conditions for its formation from the antialdoxime have not yet been determined. It is deposited from benzene in colourless crystals melting at 126°. An isomeric derivative could not be obtained.

Orthomethoxybenzantialdoxime is not altered by the successive action of hydrogen chloride and soda. The following carbanilido- and carboto-luido-derivatives were prepared by the action of phenylic isocyanate and of the tolylic isocyanates on the “syn-” and “anti-”

aldoximes in ethereal solution at ordinary temperatures; the isomeric modifications were obtained by heating the additive compounds with ether. Carbanilidorthomethoxybenzantialdoxime, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \overset{\text{CH}}{\underset{\text{||}}{\text{N}}}\text{HPh} \cdot \text{CO} \cdot \text{O} \cdot \text{N}$,

has been previously described, and exists only in one modification.

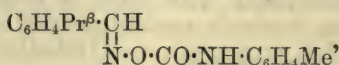
Carborthotoluidorthomethoxybenzantialdoxime, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \overset{\text{CH}}{\underset{\text{||}}{\text{N}}}\text{H} \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{O} \cdot \text{N}$,

crystallises in colourless prisms, and melts at 106° . On hydrolysis with soda, the oxime is regenerated. In addition to the above crystals, an oily liquid is formed in small quantity; this may be an isomeric modification, as on treatment with soda it yields orthoditolylcarbamide, orthotoluidine, and the original oxime. Carboparatoluidorthomethoxybenzantialdoxime crystallises in colourless, transparent needles melting at 131° ; a second modification could not be obtained.

The additive compounds of cuminantialdoxime appear only to exist in one modification, and do not yield derivatives of the synaldoxime.

Carbanilidocuminantialdoxime, $\text{C}_6\text{H}_4\text{Pr}^\beta \cdot \overset{\text{CH}}{\underset{\text{||}}{\text{N}}}\text{HPh} \cdot \text{CO} \cdot \text{O} \cdot \text{N}$, crystallises in thick, colourless prisms melting at 89° . Carborthotoluidocuminantialdoxime, $\text{C}_6\text{H}_4\text{Pr}^\beta \cdot \overset{\text{CH}}{\underset{\text{||}}{\text{N}}}\text{H} \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{O} \cdot \text{N}$, is deposited in small needles, and melts at 70° .

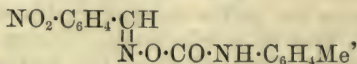
Carboparatoluidocuminantialdoxime crystallises in colourless plates melting at 115° . Carboparatoluidocuminosynaldoxime,



is deposited in pale yellow needles; it becomes colourless at $70-75^\circ$, and melts at 113° with decomposition. The isomeric modification crystallises in colourless needles, and melts at 120° .

Paranitrobenzantialdoxime gives neither isomeric additive products with isocyanates, nor derivatives of the synaldoxime. Carborthotolu-

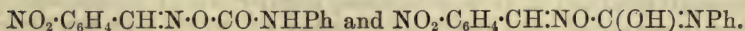
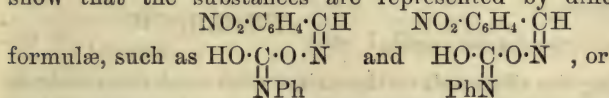
idoparanitrobenzantialdoxime, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \overset{\text{CH}}{\underset{\text{||}}{\text{N}}}\text{H} \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{O} \cdot \text{N}$, crystallises in yellow needles melting at about 183° . Carboparatoluidoparanitrobenzantialdoxime forms slender, yellowish needles, and melts at 154° . Carborthotoluidoparanitrobenzosynaldoxime,



is deposited in yellow, rhombic plates; it begins to decompose at 100° , and melts at about 185° . Carboparatoluidoparanitrobenzosynaldoxime crystallises in transparent, pale yellow plates; it softens under 100° and melts at about 176° with decomposition.

Metanitrobenzantialdoxime gives isomeric additive products with isocyanates, but does not yield "syn-" derivatives. Carbanilidometanitrobenzantialdoxime (m. p. 105°) has been previously described by Goldschmidt and Ernst (Abstr., 1890, 1261); on treatment with soda,

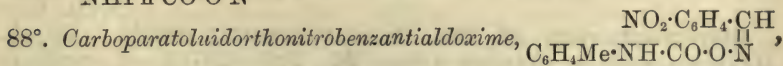
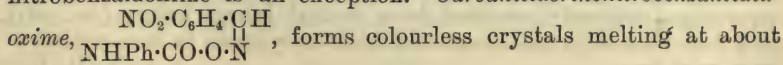
it yields diphenylcarbamide, aniline, and the oxime; by the action of ether at ordinary temperatures, it is slowly converted into an isomeric modification; the change occurs more rapidly in presence of hydrogen chloride, or on boiling with alcohol or benzene. The compound crystallises in small, yellow needles, melts at 139° with decomposition, and, on hydrolysis, yields the same substances as its isomeride. *Carboparatoluidometanitrobenzantialdoxime* forms small, yellow, transparent needles melting at about 185° , with previous softening at about 96° . The second modification, prepared in a similar manner to the corresponding carbanilido-derivative, crystallises in yellow, transparent prisms, and melts at 132° . Both compounds, on hydrolysis, yield paratoluidine, paradiethylcarbamide, and regenerated oxime. *Carborthotoluidometanitrobenzantialdoxime* appears to exist in one form only; it forms yellow crystals, which melt at 138° with evolution of gas and previous softening. *Carboparatoluidometanitrobenzosynaldoxime* crystallises in yellow, microscopic needles; it begins to decompose at $100-103^{\circ}$, and melts at 185° . The authors are unable to explain the occurrence of two isomeric carbanilidometanitrobenzantialdoximes (see above); it is possible that the nitrogen atom of the NH group is asymmetric, although both compounds are optically inactive; on chemical grounds, there appears to be no evidence to show that the substances are represented by different structural



The above results prove that paramethoxybenzantialdoxime differs from benzantialdoxime, but resembles the corresponding thiophen- and furfur-aldoximes in yielding "syn-" additive compounds with the tolylic isocyanates. Further, that the formation of isomeric carbanilido-derivatives, which was first observed by Beckmann in the case of carbanilidobenzosynaldoxime (Abstr., 1891, 193), occurs with tolerable frequency.

J. B. T.

Isomeric Orthonitrobenzaldoximes. By H. GOLDSCHMIDT and W. H. VAN RIETSCHOTEN (*Ber.*, 26, 2100—2103).—It has been shown that many ortho-substituted benzantialdoximes are not converted into the isomeric synaldoximes by Beckmann's method; to this rule orthonitrobenzaldoxime is an exception. *Carbanilidorthonitrobenzantialdoxime*,



is prepared either from the pure oxime, or by heating a mixture of the "anti-" and "syn-" oximes with paratolylic isocyanate in benzene solution; it crystallises in small, colourless needles, melts at 139° , and on treatment with soda yields orthonitrobenzantialdoxime, paratoluidine, and in small quantity paradiethylcarbamide. *Orthonitro-*

benzosynaldoxime, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{smallmatrix} \text{CH} \\ \text{NOH} \end{smallmatrix}$, is obtained by treatment of the anti-aldoxime with hydrogen chloride in ethereal solution; the resulting salt, which melts at 87° , is decomposed with soda, and the product crystallised from benzene. It melts at 136° , and is somewhat more sparingly soluble than the antialdoxime, into which it is readily converted. The *carbanilido-derivative*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{smallmatrix} \text{CH} \\ \text{N} \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh} \end{smallmatrix}$, is deposited in yellow prisms melting at 91° , with evolution of gas. The *carboparatoluidide*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{smallmatrix} \text{CH} \\ \text{N} \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me} \end{smallmatrix}$, resembles the preceding compound, and melts at 93° with decomposition. *Orthonitrobenzaldoxime methyl ether*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} < \begin{smallmatrix} \text{NMe} \\ \text{O} \end{smallmatrix}$, is prepared by the action of sodium methoxide and methylic iodide on the synaldoxime in methyl alcoholic solution at ordinary temperatures, and is deposited from ether in long, yellow crystals melting at 92° . The constitution of the compound is proved by its resolution into orthonitrobenzaldehyde and methylhydroxylamine when heated with dilute sulphuric acid. By the action of hydriodic acid at 100° under pressure, methylamine is formed.

Orthonitrobenzosynaldoxime methyl ether $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{smallmatrix} \text{CH} \\ \text{N} \cdot \text{OMe} \end{smallmatrix}$, is obtained by treating the silver salt of the oxime with methylic iodide in ethereal solution; it is a colourless, slightly viscid liquid, and is readily converted into the "anti-" ether (m. p. 58°) by the action of hydrogen chloride. J. B. T.

Hydrocinnamaldoxime: A Correction. By W. DOLLFUS (*Ber.*, 26, 1970—1972).—In a former paper (*Abstr.*, 1892, 1174) the author described the preparation of hydrocinnamaldehyde from chromyl chloride and propylbenzene, quite overlooking v. Miller's observation (*Abstr.*, 1190, 978) that the product of this reaction is methyl benzyl ketone. He now describes the following derivatives of hydrocinnamaldehyde, a sample of this compound, prepared by distilling calcium hydrocinnamate with calcium formate, having been furnished him by v. Miller.

Hydrocinnamaldoxime, $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{NOH}$, crystallises from alcohol in long prisms, and melts at $93\text{--}94.5^\circ$; it yields hydrocinnamonnitrile when treated with acetic anhydride or acetic chloride. The substance previously prepared from methyl benzyl ketone (*loc. cit.*), and described as hydrocinnamonnitrile, is now found to be a mixture.

A. R. L.

Stereoisomerism of the Benzhydroxamic acids. By A. HANTZSCH and A. WERNER (*Ber.*, 26, 2069—2070).—A reply to Lossen (this vol., i, 572).

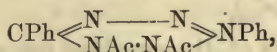
Action of Hydrazine on Imido-ethers. By A. PINNER (*Ber.*, 26, 2126—2135).—By the action of hydrazine (3 mols.) on benzimide ethyl ether (2 mols.) in dilute alcoholic solution at ordinary

temperatures, numerous products are formed, of which six have been isolated in the manner described by the author, taking advantage of differences in their basicities and solubilities.

Dibenzonylhydrazidine, $C_{14}H_{14}N_4$, crystallises from chloroform in yellowish, lustrous plates melting at 202° , without decomposition. It is not acted on by oxidising agents at ordinary temperatures, and probably, therefore, has the formula $N_2(CPh \cdot NH_2)_2$, rather than $N_2H_2(CPh \cdot NH)_2$. The *hydrochloride* crystallises in lustrous needles; the *platinochloride* in yellow prisms. On treatment with nitrous acid, the hydrazidine is converted into dibenzoylhydrazine. This hydrazidine is accompanied by a second basic compound, $C_{21}H_{21}N_5O$, which occurs in small quantity, is almost insoluble in chloroform, and crystallises in silky, lustrous needles melting at 170° . Its investigation is incomplete. The *hydrochloride* is readily soluble; the *platinochloride* is amorphous.

Benzenylimidonitrile, $CPh \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix}$, is probably formed by elimination of ammonia from the intermediate compound, $NH \cdot CPh \cdot NH \cdot NH_2$; it is readily soluble in dilute alcohol, crystallises in colourless plates, begins to soften at about 240° , and melts at 258° . The *hydrochloride* and *platinochloride* are crystalline.

Diphenyldihydrotetrazine, $CPh \begin{smallmatrix} \text{N} \text{---} \text{N} \\ \text{NH} \cdot \text{NH} \end{smallmatrix} CPh$, is the chief product of the reaction, and crystallises in long, colourless, slender needles; the compound exhibits feebly basic properties, and is converted into the corresponding tetrazine (see below) by heating, or by the action of air or oxidising agents. The *diacetyl derivative*,



forms colourless, crystalline plates, and melts at $228\text{--}229^\circ$.

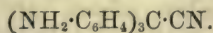
Diphenyltetrazine, $CPh \begin{smallmatrix} \text{N} \cdot \text{N} \\ \text{N} \cdot \text{N} \end{smallmatrix} CPh$, is readily prepared from the preceding compound by oxidation; it forms flat, bluish-red prisms, and melts at 192° . It is soluble in concentrated sulphuric acid with a red coloration, and is precipitated on dilution; it is not acted on by a mixture of sulphuric acid and fuming nitric acid at ordinary temperatures. By treatment with reducing agents the dihydrogen derivative is regenerated.

A compound, $C_{14}H_{13}N_3$, which it is proposed to term *dibenzimidine*, $NH(CPh \cdot NH)_2$ (compare Abstr., 1892, 1110), has also been obtained. After treatment with water, it crystallises from ethylic acetate with $2H_2O$ in prisms melting at 80° ; the anhydrous substance melts at 131° . It is suggested that this compound is formed from dibenzonylhydrazidine by the action of alkali in a manner similar to that in which the osotetrazones are converted into the osotriazones. The action of hydrazine on acetimidoethyl ether is under investigation; the products are extremely volatile and difficult to isolate.

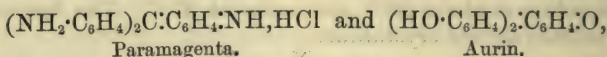
J. B. T.

Constitution of Hydrocyanorosaniline and of Magenta. By E. FISCHER and W. L. JENNINGS (*Ber.*, 26, 2221—2225).—E. and O.

Fischer (*Annalen*, 194, 275) looked on hydrocyanopararosaniline as the triamido-derivative of a cyanotriphenylmethane, but were unable to prepare the latter by the aid of the diazo-reaction. When, however, the base is diazotised, and then treated by the Sandmeyer-Gattermann method, triphenylacetone nitrile, $\text{CPh}_3\cdot\text{CN}$ is readily obtained. It melts at 127° , and is identical in its properties with the substance prepared from triphenylmethylic bromide and mercuric cyanide. Hydrocyanopararosaniline has therefore the constitution



Rosenstiehl (Abstr., 1893, i, 332) has proposed for the salts of pararosaniline the formula $(\text{NH}_2\cdot\text{C}_6\text{H}_4)_3\text{C}\cdot\text{X}$, so that in view of the close analogy of similarly constituted chlorine and cyano-derivatives, the pararosaniline salts should be very similar to hydrocyanopararosaniline. The opposite of this is, however, the case, and the Rosenstiehl formulæ, moreover, do not exhibit the relations of pararosaniline to aurine, and of magenta to rosolic acid. On the other hand the formulæ proposed by Nietzki (*Chemie der organischen Farbstoffe*, 1889, 88),



agree with all the observed facts, and, in fact, are simply related to the older formulæ, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{C}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2 \\ \text{NH}, \text{HCl} \end{smallmatrix}$ and $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{C}(\text{C}_6\text{H}_4\cdot\text{OH})_2 \\ \text{O} \end{smallmatrix}$, in the same way as the diketone formula, $\text{O}:\text{C}_6\text{H}_4:\text{O}$ for quinone, is to the peroxide formula, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$.

The chemical analogy of the rosaniline compounds to the quinones is very striking, and was pointed out long ago by Graebe and Caro (*Annalen*, 179, 184); the combination of the rosaniline salts with three additional molecules of acid, which led Rosenstiehl to propose his new formula, is quite analogous to the combination of quinone with hydrochloric acid. The constitution of the rosaniline salts containing 4 mols. of acid cannot, however, be considered as yet settled.

The application of the Sandmeyer-Gattermann method to the diazo-compound of pararosaniline has led to the conversion of this substance into triphenylcarbinol, and thus confirmed the view taken by E. and O. Fischer, who were unable at the time of their research to accomplish this transformation. A. H.

Action of Amides on Benzaldehyde. By K. BÜLOW (*Ber.*, 26, 1972—1974).—*Benzylidenediformamide*, $\text{CHPh}(\text{NH}\cdot\text{CHO})_2$, is obtained by heating benzaldehyde and formamide together on the water bath for 24 hours; it crystallises from water in white, silky needles, melts at $149\text{--}150^\circ$, is insoluble in ether, and reduces alkaline silver solutions. If heated with water in a sealed tube at 100° , or treated with 0.1 per cent. hydrochloric acid at the ordinary temperature, it is hydrolysed into its components. When benzaldehyde

is boiled with formamide in a reflux apparatus for two hours, tetraphenylpyrazine (m. p. 246—247°), together with other compounds, is obtained. Roth's benzylidenediacetamide (*Annalen*, **154**, 72) is formed by heating benzaldehyde with acetamide on the water bath; 100 parts of water dissolve 3 parts at 100°, and 1 part at 20°. When benzaldehyde is boiled for 5—7 hours with acetamide, tetraphenylpyrazine and other compounds are obtained. Benzylidenedibenzamide (Roth, *loc. cit.*) is formed, together with other compounds and a small quantity of tetraphenylpyrazine, when benzaldehyde is boiled with benzamide.

A. R. L.

Iodoso-compounds, a Reply to C. Willgerodt. By V. MEYER (*Ber.*, **26**, 2118—2122).—A polemical paper criticising generally Willgerodt's work on iodoso-compounds, and referring particularly to his last communication on the subject (this vol., i, 503). Iodosobenzoic acid is very different in appearance and properties from iodoxybenzoic acid; the former crystallises in light, silvery, lustrous plates, melts without detonation, has no sour taste, and is more phenolic than acidic in properties. Iodoxybenzoic acid forms dense, granular crystals, has a strongly-marked acid reaction and taste, and explodes on heating. The specimen of iodosobenzoic acid which undergoes decomposition at 244° is, contrary to Willgerodt's suggestion, the purest form of the acid hitherto prepared, and it is not altered by crystallisation from glacial acetic acid. The author has prepared a toxic base containing iodine, but free from nitrogen, from iodosobenzene, and from iodoxybenzene; its salts resemble those of thallium; the sulphate is soluble; the haloïd salts are insoluble. The base, which is liberated by the action of moist silver oxide on the salts, is soluble in water, and has a strongly alkaline reaction. It is being further investigated.

J. B. T.

Hydrogenised Paratoluic acids. By A. EINHORN and R. WILLSTÄTTER (*Ber.*, **26**, 2009—2010).—When paramethylenehydrobenzoic acid (this vol., i, 378) is reduced at the ordinary temperature, it is converted into *tetrahydroparatoluic acid*. The latter solidifies to colourless needles when cooled in a freezing mixture, but is liquid at the ordinary temperature; it boils at 250—253°, has a characteristic pungent odour, and instantly decolorises a solution of permanganate. The *calcium* salt crystallises in white needles with 4H₂O; the *copper* salt forms deep blue aggregates of thin tablets with 2H₂O; the *methylic* salt boils at 210—220°; and the *amide* melts at 157—158°. *Paramethylenehydrobenzamide* melts at 125·5°.

When tetrahydroparatoluic acid is boiled with a solution of sodium hydroxide, it is converted into an *isomeride*; this boils at 254—260°, and solidifies readily. It crystallises from alcohol in colourless leaflets, is devoid of odour, and melts at 45—47°. The *calcium* salt, with 4H₂O, differs in solubility from that of the isomeride; the *methylic* salt resembles the isomeric compound; and the *amide* melts at 134—135°.

A. R. L.

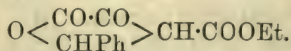
Hexahydroisophthalic acid. By V. VILLIGER (*Annalen*, **276**, 255—265).—Isophthalic acid is prepared by treating boiling meta-

xylene with dry bromine (2 mols.), digesting the crystalline product on the water bath with an excess of alcoholic potassium acetate, and heating the diacetate thus obtained on the water bath with an alkaline solution of potassium permanganate. The dry barium salt prepared from the crude acid is extracted with cold water, which dissolves the barium metatoluate. The yield of pure isophthalic acid is 100 per cent. of the metaxylene.

To reduce isophthalic acid, it is dissolved in a solution of sodium carbonate (70 grams) in water (300 c.c.), and treated in presence of a current of carbonic anhydride with about 2 kilos. of a 3 per cent. sodium amalgam at 40–50°, the amalgam being added in the course of two days, in portions of 50 grams at a time. The crude product is heated at 100° in a sealed tube with concentrated hydrobromic acid for 20 hours, and the hydrobromide treated with zinc dust and acetic acid, or preferably with sodium amalgam in presence of carbonic anhydride. A mixture of the two hexahydroisophthalic acids, synthesised by W. H. Perkin, jun. (Trans., 1891, 798), is obtained; they can be separated by following his directions, and agree in every particular with his description.

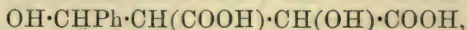
The paper concludes with some remarks by v. Baeyer, who draws attention to the fact that the hexahydro-derivatives of all three benzenecarboxylic acids resemble the aliphatic acids containing the same number of carbon atoms between the carboxyl groups (see also Perkin, *loc. cit.*).
A. R. L.

Action of Benzaldehyde on Ethylic Oxalacetate. By W. WISLICENUS (*Ber.*, 26, 2144–2147).—The product of this reaction is not ethylic hydrogen benzylideneoxalacetate, as previously supposed (this vol., i, 146), for it does not take up bromine, nor yield an ethylic salt; it is doubtless *ethylic ketophenylparaconate*,



Its *sodium derivative*, $\text{C}_{13}\text{H}_{11}\text{O}_5\text{Na}$, is a white crystalline substance, and, when reduced with sodium amalgam, it yields *ethylic phenylhydroxyparaconate*, $\text{O} < \begin{array}{c} \text{CO} \cdot \text{CH}(\text{OH}) \\ \text{CHPh} \end{array} > \text{CH} \cdot \text{COOEt}$, which crystallises in small, white needles, melting at 86–88°.

The last substance, when boiled with caustic soda, yields the sodium salt of *phenylhydroxyvitamalic acid*,



the *silver salt* of which, $\text{C}_{11}\text{H}_{10}\text{O}_6\text{Ag}_2$, is a white powder.

C. F. B.

Action of Formaldehyde on Benzenesulphonamide. By A. MAGNUS-LEVY (*Ber.*, 26, 2148–2150).—When an alcoholic solution of benzenesulphonamide is heated with a 40 per cent. aqueous solution of formaldehyde and a little hydrochloric acid, *tribenzenesulphonetrimethylenetriimide*, $\text{C}_3\text{H}_6\text{N}_3(\text{SO}_2\text{Ph})_3$, is formed, together with the analogous dimolecular compound $\text{C}_2\text{H}_4\text{N}_2(\text{SO}_2\text{Ph})_2$. The former crystallises in white needles, melts at 217°, and is nearly insoluble in

hot alcohol; the latter forms lustrous needles, melts at 132° , and dissolves readily in alcohol. These compounds contain respectively a 6- and a 4-membered ring, consisting of alternate carbon and nitrogen atoms.

C. F. B.

Action of Phosphorus Pentachloride on Orthobenzoicsulphinide. By J. A. JESURIN (*Ber.*, 26, 2286—2298).—The compound described by Brackett (*Abstr.*, 1888, 282), obtained by the successive action of phosphorus pentachloride and methyl alcohol on orthobenzoicsulphinide, is shown by the author to be *methyl orthosulphaminebenzoate*, $\text{COOMe} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{NH}_2$. It is prepared by heating orthobenzoicsulphinide for two hours at the ordinary pressure at 70 — 75° with phosphorus pentachloride, and pouring the product into well-cooled methyl alcohol; or by passing hydrogen chloride into a solution of orthobenzoicsulphinide in methyl alcohol. It melts at 125 — 126° , and, like the corresponding ethylic compound (*Abstr.*, 1881, 816; 1888, 367), yields salts of orthobenzoicsulphinide when boiled with alkalis and ammonia.

When orthobenzoicsulphinide is heated with phosphorus pentachloride at 70 — 75° in a sealed tube, *orthocyanobenzenesulphonic chloride*, $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Cl}$, is obtained; it separates from benzene in stout crystals, melts at 69 — 70° , and yields *orthocyanobenzenesulphonic acid* when boiled with water; this acid could not be isolated, but the *sodium salt*, $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na} + \text{H}_2\text{O}$, crystallises in prisms. If orthocyanobenzenesulphonic chloride is heated in a sealed tube at 95 — 100° with a little water, the eliminated hydrogen chloride converts the orthocyanobenzenesulphonic acid initially formed into orthobenzaminesulphonic acid (*Abstr.*, 1889, 709); whilst at 180° the action proceeds further, and *ammonium hydrogen orthosulphobenzoate*,



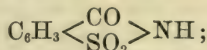
is formed, a fact which shows that orthosulphobenzoic acid is a stronger acid than hydrochloric acid; indeed, when concentrated solutions of orthosulphobenzoic acid and ammonium chloride are heated together, ammonium hydrogen orthosulphobenzoate is obtained. When orthocyanobenzenesulphonic chloride is heated with alcohol, orthobenzaminesulphonic acid, ethylic chloride, and ether are formed. The *sulphonamide*, $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{NH}_2$, is obtained by treating the chloride with a solution in benzene containing exactly twice the molecular proportion of ammonia; it crystallises in leaflets, melts at 260° , and is almost insoluble in benzene, but fairly soluble in cold water and alcohol. It dissolves in aqueous ammonia, and when the solution is heated, an isomeric compound, $\text{C}_6\text{H}_4 \cdot \text{C}(\text{NH}_2) \text{SO}_2 \text{N}$, separates (see below); the third isomeride (diimide) is probably also formed, but it appears to decompose when boiled with water into orthobenzoicsulphinide. The *anilide*, $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NHPh}$, is obtained by treating orthocyanobenzenesulphonic chloride with aniline; it melts at 150 — 152° ; whilst by heating the chloride with aniline in a sealed tube at 150° , an isomeric compound, $\text{C}_6\text{H}_4 \cdot \text{C}(\text{NHPh}) \text{SO}_2 \text{N}$, is obtained, insoluble in benzene, and not melting at 315° , together with a com-

pound, $\text{C}_6\text{H}_4\langle\text{C}(\text{NPh})\rangle\text{SO}_2\text{—}$, which crystallises from benzene in yellow needles, and melts at $187\text{--}189^\circ$.

The *chloride*, $\text{C}_6\text{H}_4\langle\text{CCl}\rangle\text{SO}_2\text{—}$, is obtained by heating orthobenzoic-sulphinide at 180° under ordinary pressure with phosphorus pentachloride (2 mols.); it crystallises from benzene in small needles, melts at $143\text{--}145^\circ$, and yields orthobenzoicsulphinide when treated with water. The *ethyl ether*, $\text{C}_6\text{H}_4\langle\text{C}(\text{OEt})\rangle\text{SO}_2\text{—}$, is obtained by boiling the chloride with absolute alcohol; it crystallises in flat needles, melts at $217\text{--}218^\circ$, and decomposes when heated with water at 150° in a sealed tube into orthobenzoicsulphinide and orthosulphaminebenzoic acid; at $280\text{--}300^\circ$ the product is principally ammonium hydrogen orthosulphobenzoate. The *methyl ether* melts at $182\text{--}183^\circ$. The *amide*, $\text{C}_6\text{H}_4\langle\text{C}(\text{NH}_2)\rangle\text{SO}_2\text{—}$, is prepared by heating the analogous chloride with ammonium carbonate, or by heating it with a solution of ammonia in benzene; it is likewise obtained as above mentioned, and also by treating orthocyanobenzenesulphonic chloride with an excess of ammonia, or the last-described ethyl ether with alcoholic ammonia; it is almost insoluble in cold water, but separates from hot water in small, stout crystals, and does not melt at 300° . When heated with aniline in a sealed tube at $170\text{--}180^\circ$, it yields the anilide described above.

Orthochlorobenzonitrile, $\text{CN}\cdot\text{C}_6\text{H}_4\text{Cl}$ (Henry, *Ber.*, 2, 492), is obtained by heating orthobenzoicsulphinide with phosphoric chloride at 230° .

The author considers that the following experiments justify the assumption that orthobenzoicsulphinide has the constitution



the pseudo-modification, $\text{C}_6\text{H}_4\langle\text{C}(\text{OH})\rangle\text{SO}_2\text{—}$, appears to be incapable of existence, although several of its derivatives have been prepared.

A. R. L.

Action of Phosphorus Pentachloride on Orthobenzoicsulphinide. By C. FAHLBERG (*Ber.*, 26, 2299).—The experiments described in Jesurin's paper (preceding abstract) were made at the author's suggestion. Now that technical orthobenzoicsulphinide can be readily purified (Eng. Pat. of 1891, No. 22,787), additional facilities are offered for its study.

A. R. L.

Synthesis of Indene and Hydrindene. By W. H. PERKIN, Jun., and G. RÉVAY (*Ber.*, 26, 2251—2254).—Indene is obtained by the distillation of barium hydrindenecarboxylic acid either alone or in presence of sodium methoxide. This synthetic indene has most of the properties of the indene isolated by Krämer and Spilker from coal tar (Abstr., 1891, 205), and gives the same hydrindene on reduction. It differs, however, in sp. gr., refractive index, and magnetic rotation, which may be due to traces of impurities; but the authors

point out that two isomeric indenenes are possible, of the formulæ $C_6H_4<\begin{smallmatrix} CH \\ CH_2 \end{smallmatrix}>CH$ and $C_6H_4<\begin{smallmatrix} CH \\ CH \end{smallmatrix}>CH_2$, which would yield the same hydrindene on reduction. Both products boil at 180° , and give a reddish-brown resin with sulphuric acid.

Methylic hydrindenecarboxylate, $C_9H_9\cdot COOMe$, is a colourless oil, boils at 170° under 60 mm. pressure, and, after some time, solidifies in tabular crystals.

Hydrindenecarboxylic chloride, obtained by the action of phosphorus pentachloride on the acid, boils at 180° under 100 mm. pressure, crystallises on cooling in large, colourless crystals, and melts at 38° . The *amide* crystallises in lustrous prisms, and melts at 178° . The *anilide* melts at 182° .

Tetrabromhydrindenecarboxylic acid, $C_9H_5Br_4\cdot COOH$, is obtained by the action of bromine vapour on hydrindenecarboxylic acid. It crystallises in needles, and melts at $248\text{--}250^\circ$.

Indenecarboxylic acid is obtained by the action of bromine on a solution of hydrindenecarboxylic acid in chloroform at 100° . It crystallises from acetic acid in needles, softens at 220° , and melts at 230° .

Hydrindene methyl ketone, $C_6H_4<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>CH\cdot COMe$, is obtained by the action of zinc methide on an ethereal solution of hydrindenecarboxylic chloride. It boils at $180\text{--}185^\circ$ under 70 mm. pressure. The *oxime* crystallises in large, lustrous prisms, and melts at 127° .

Hydrindenemethylcarbinol, $C_9H_9\cdot CHMe\cdot OH$, obtained from the ketone by reduction with sodium and alcohol, melts at 45° , and boils at $185\text{--}190^\circ$ under 80 mm. pressure. The *acetate* boils at $188\text{--}190^\circ$ under 70 mm. pressure.

Hydrindene ethyl ketone melts at 28° and boils at $188\text{--}190^\circ$ under 80 mm. pressure. The *oxime* melts at 105° . *Hydrindeneethylcarbinol* boils at 192° under 80 mm. pressure, crystallises from alcohol in beautiful, colourless needles, and melts at 63° . The *acetate* boils at 210° under 80 mm. pressure.

Hydrindene phenyl ketone, obtained by the action of benzene on hydrindenecarboxylic chloride in the presence of aluminium chloride, crystallises in slender needles, and melts at 107° .

Bromine acts very readily on a solution of hydrindene in chloroform with the formation of *dibromhydrindene*, which boils at $180\text{--}185^\circ$ under 50 mm. pressure. If, however, the crude product is distilled at the ordinary pressure, hydrogen bromide and *monobromhydrindene* are obtained. The latter boils at $242\text{--}244^\circ$, and, when oxidised with nitric acid, yields 1 : 2 : 4-bromophthalic acid melting at $162\text{--}164^\circ$, and yielding an anhydride which melts at 106° . E. C. R.

Conversion of Carbazole into Indole. By C. U. ZANETTI (*Ber.*, 26, 2006—2008).—Tetrahydrocarbazole is obtained more readily by boiling carbazole with sodium and amyl alcohol than by Graebe and Glaser's method (*Annalen*, 163, 352). When tetrahydrocarbazole is fused with potash, α -indolecarboxylic acid (Ciamician and Zatti, *Abstr.*, 1888, 957) is produced. A. R. L.

"Hydrocoton" and its Derivatives. By O. HESSE (*Annalen*, 276, 328—342; compare Ciamician and Silber, *Abstr.*, 1892, 62, and 873; this vol., i, 409 and 417).—*Bromhydrocoton*, $C_9H_{11}BrO_3$, forms colourless needles, and melts at 99° ; and the *dibromo*-derivative, $C_9H_{10}Br_2O_3$, crystallises in white leaflets, and melts at 133° . The compound obtained by oxidising hydrocoton with chromic acid is metadimethoxyquinone, first prepared by Hofmann (compare Ciamician and Silber, *loc. cit.*; Will, *Abstr.*, 1888, 1089). The author's experiments confirm Ciamician and Silber's conclusion, that "hydrocoton" is trimethylphloroglucinol; he finds that when hydrocoton is heated with concentrated hydrochloric acid in a sealed tube at 85° , small quantities of phloroglucinol are obtained together with phloroglucide and *phloroglucan*, $C_6H_4O_2$, a compound which crystallises from water in white needles, and melts at 118° ; the chief portion of the product consists, however, of "*triphloroglucinol chloride*," $C_{18}H_3ClO_6 + 2\frac{1}{2}H_2O$, which crystallises in bright orange needles, and is soluble in alkalis and alcohol, but insoluble in water. When boiled with water, *triphloroglucide*, $C_{18}H_{14}O_7 + 2H_2O$, is formed; it is a dark yellow, hygroscopic, crystalline powder.

The compound obtained by methylating hydrocotoin is benzoylhydrocoton, as Ciamician and Silber have shown. The author has isolated an isomeride, *i*-benzoylhydrocoton, $C_6H_2(OMe)_3 \cdot COPh$ [$(OMe)_3 : COPh = 1 : 3 : 5 : 2$], during the crystallisation of crude paracotoin from alcohol; it forms colourless leaflets, and melts at 115° .

A. R. L.

Phenylacridine. By A. CLAUS and J. BECKENKAMP (*J. pr. Chem.*, [2], 48, 222—225).—The intense yellow prisms of phenylacridine obtained by crystallisation from alcohol, and the colourless leaflets obtained by sublimation, are found to be crystallographically identical. Both belong to the monoclinic system, $a : b : c = 0.9915 : 1 : 1.0257$; $\beta = 27^\circ 33'$.

E. C. R.

The Aluminium Chloride Synthesis. By H. BILTZ (*Ber.*, 26, 1960—1962).—In carrying out a Friedel-Crafts synthesis with aluminium chloride, it is sometimes better, for instance, in the preparation of triphenylmethane, to use pure chloride prepared from the metal; in other cases, such as the preparation of tetraphenylethane from stilbene dibromide and benzene, a better yield is obtained when the ordinary commercial chloride is used. C. F. B.

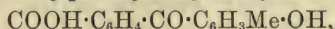
Action of Chloral on Benzene in the presence of Aluminium Chloride. By H. BILTZ (*Ber.*, 26, 1952—1960).—When a mixture of benzene, carbon bisulphide, and chloral is heated with pure aluminium chloride, there are obtained, in addition to tetraphenylethane and diphenyldichlorethylene, two new substances, both in small quantity.

The first of these, *triphenylvinyl alcohol*, $CPh_2 \cdot CPh \cdot OH$, forms silky, tabular, monoclinic crystals, melts at 136° , and is converted by oxidation into benzophenone and benzoic acid, and by the action of sodium ethoxide into diphenylmethane and benzoic acid. The other, which is a *hydrocarbon* (C 94.24, H 5.78 per cent.), forms silky needles melting at 233° , and is converted by oxidation into a substance which melts at 166 — 167° , and yields colourless crystals. C. F. B.

Phthaleïnoxime. II. By P. FRIEDLÄNDER and A. STANGE (*Ber.*, 26, 2258—2264; compare this vol., i, 273).—Those phenolphthaleïns which, when dissolved in alkalis, yield salts with formation of a quinone derivative, very easily combine with hydroxylamine. Thus, the intense blue to brownish-violet alkaline solution of the colourless tetrabromophenolphthaleïns, of orthocresolphthaleïn, and of quinol-, catechol-, and orcinol-phthaleïn react very easily with hydroxylamine; whereas the yellow solutions of di- and tetra-nitrophenolphthaleïn do not. The reddish-yellow solution of fluoresceïn, which is very similar to the colour of its salts, and therefore probably contains fluoresceïn of the same constitution, does not react with hydroxylamine. However, the intense violet solution of fluoresceïn and of eosin in concentrated alkali does react with hydroxylamine.

Tetrabromophenolphthaleïnoxime is obtained by treating an alkaline solution of tetrabromophenolphthaleïn with hydroxylamine hydrochloride. It forms amorphous flocks, which cannot be crystallised. When heated in alcoholic solution with dilute sulphuric acid, it yields *dibromoparahydroxyorthobenzoïlbenzoic acid* and dibromamidophenol sulphate. The former crystallises from acetic acid in colourless prisms, and melts at 246—248° with decomposition. The latter, when treated with sodium hydrogen carbonate, yields bromoparamidophenol, which melts at 190° with decomposition, and crystallises in slender needles.

Orthocresolphthaleïnoxime, when treated with sulphuric acid in a similar way, yields *methylparahydroxybenzoïlbenzoic acid*,

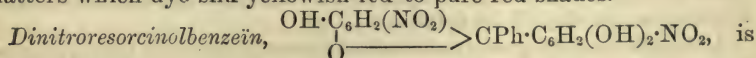


and paramidorthocresol. The former crystallises in needles, and melts at 230° with decomposition. The latter, on account of its instability, cannot be conveniently separated, but is easily converted into its *dibenzoïl* derivative, which crystallises in white, interlacing needles, and melts at 194°. E. C. R.

Condensation Products of Monobasic Acids with Resorcinol.

By G. COHN (*Ber.*, 24, 2064—2068).—This paper contains a description of the condensation products of resorcinol with benzoic, phenylacetic, and cinnamic acids; a more detailed paper is to be published at a later date. Condensation takes place when the acid is fused with resorcinol in the presence of zinc chloride or phosphoric anhydride.

Resorcinolbenzeïn, previously prepared by Döbner (*Ber.*, 13, 610), is formed from resorcinol and benzoic acid. It forms an unstable compound with hydrochloric acid, and is readily acted on by bromine. According to the amount of halogen used and the temperature of the bromination, *di*-, *tetra*-, or *penta-bromoresorcinolbenzeïn* is produced. All these substances have been isolated, and are fluorescent colouring matters which dye silk yellowish-red to pure red shades.



formed by the action of fuming nitric acid in the cold on resorcinolbenzeïn. It crystallises in fascicular groups of brittle, reddish-

yellow needles, and deflagrates above 250° without melting. It dyes silk and wool a beautiful orange-yellow. Its brown alkaline solution is coloured red on boiling with an excess of caustic potash.

Resorcinolphenylaceteïn, $\text{OH} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ | \end{smallmatrix} \text{---} > \text{C}(\text{CH}_2\text{Ph}) \cdot \text{C}_6\text{H}_3(\text{OH})_2$, is prepared from phenylacetic acid, and forms microscopic, brown, rhombic plates melting at 266—268°. It is only slightly soluble in the usual solvents, but dissolves easily in pyridine and similar substances. In alkaline solution, it shows an intense, brilliant, green fluorescence. From such solutions, it is precipitated by carbonic anhydride in yellowish-red flakes. On wool and silk, it produces yellow shades. On heating with acetic anhydride, a *diacetyl* derivative is formed.

Tetrabromoresorcinolphenylaceteïn, $\text{C}_6\text{HBr}_2 \begin{smallmatrix} \text{O} \\ | \end{smallmatrix} \text{---} > \text{C}(\text{CH}_2\text{Ph}) \cdot \text{C}_6\text{HBr}_2(\text{OH})_2$, formed by the direct action of bromine, melts at 236°, and closely resembles ordinary eosin prepared from phthalic acid. The *silver salt* is a deep red precipitate.

Tetrabromoresorcinolhydrocinnamyleïn, prepared in a similar manner from hydrocinnamic acid, also very closely resembles eosin in properties. The nature of the eosin produced seems not to depend on the aromatic acid employed, but almost entirely on the brominated phenolic residue. When more complicated aromatic acids are used for the condensation, however, higher brominated substances of a redder shade, which contain bromine in the side chain, can be obtained. Thus, *pentabromoresorcinolphenylaceteïn*, which crystallises in groups of long, red needles, dyes silk a splendid reddish-violet. This substance is more readily soluble in neutral and alkaline solvents than the eosins are, and does not show any trace of fluorescence in alkaline solution.

Tetranitroresorcinolphenylaceteïn is a yellow, indistinctly crystalline powder, which is moderately soluble in alcohol, and dyes wool and silk brown. Its brown alkaline solution, on boiling with an excess of potash, is coloured red in the same way as that of dinitroresorcinolbenzeïn.

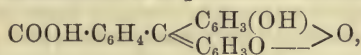
Resorcinolcinnamyleïn, prepared from cinnamic acid, is a brown, amorphous mass, which attains a green, metallic lustre at 100°. It is difficult to free it from fluorescent impurities, but, when pure, it forms a red, entirely non-fluorescent solution in alcohol. It dissolves in concentrated sulphuric acid, forming a solution which shows an intense green fluorescence. Hydrogen chloride forms an additive product which is not dissociated by water, and can be obtained in bluish-red matted needles. *Hexabromoresorcinolcinnamyleïn* crystallises in blunt needles, and is slightly soluble in acetic acid, more readily in alcohol, and very readily in alkalis. On heating, it loses hydrogen bromide. It dyes silk a violet-blue, and does not show fluorescence in any of its solutions.

Compounds analogous to resorcinolcinnamyleïn have been prepared from ortho-, meta-, and para-nitrocinnamic acid, as well as from orthohydroxycinnamic acid, but their constitutions have not yet been ascertained.

A. H.

Fluoresceïn anilide. By O. FISCHER and E. HEPP (*Ber.*, 26, 2236—2237).—When fluoresceïn is heated with aniline and aniline hydrochloride, *fluoresceïn anilide*, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C} \langle \text{C}_6\text{H}_3(\text{OH}) \rangle \text{O}$, is obtained; it crystallises from ethylic acetate in plates or flat tablets, which, on heating to 200°, become red, and give a red sublimate. It is readily soluble in glacial acetic acid, but insoluble in water. Its solutions are colourless, and, although it yields colourless solutions with alkalis, the alkaline liquid shows a strong green fluorescence. The solution in concentrated sulphuric acid has a yellowish colour and a faint green fluorescence. The compound is not decomposed by boiling with dilute acids or alkalis, but yields fluoresceïn and aniline when its concentrated alcoholic solution is boiled for some time with 40 per cent. sulphuric acid. Its *dimethyl ether* crystallises from hot alcohol in splendid, colourless, pointed prisms, and melts at 207—208°. Only the sulphuric acid solution of this substance shows any fluorescence. The ether is also very stable towards acids and alkalis.

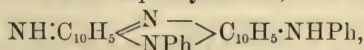
The formula of the anilide, according to the present views as to the constitution of the fluoresceïns, would be that above; from this point of view, however, it is difficult to understand how the anilide is colourless, whilst fluoresceïn itself is a coloured substance. This may be more easily understood if a quinonoid formula,



be given to fluoresceïn itself (compare Armstrong, *Proc.*, 1893, 52).

A. H.

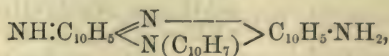
Naphthyl Red and Magdala Red. By O. FISCHER and E. HEPP (*Ber.*, 26, 2235—2236; compare this vol., i, 333, 464, 613).—Naphthyl blue (symmetrical $\alpha\beta$ -anildophenylnaphthinduline) is formed by the condensation of benzeneazophenyl- α -naphthylamine when the hydrochloride of the latter is dissolved in phenol and the solution heated (this vol., i, 338). This reaction has been applied by the authors to other azo-compounds. Benzeneazo- α -naphthylamine, when heated with phenol, yields a red colouring matter, strikingly similar in its dyeing power and fluorescence to Magdala red. This compound, $\text{NH} \cdot \text{C}_{10}\text{H}_5 \leq \text{N} \text{---} \text{NPh} \rangle \text{C}_{10}\text{H}_5 \cdot \text{NH}_2$, has proved to be the parent substance from which naphthyl violet,



and naphthyl blue, $\text{NPh} \cdot \text{C}_{10}\text{H}_5 \leq \text{N} \text{---} \text{NPh} \rangle \text{C}_{10}\text{H}_5 \cdot \text{NHPh}$, are derived, and has therefore received the name of *naphthyl red*. On treatment with concentrated hydrochloric acid under pressure, it loses ammonia, and an amidonaphthindone is formed, which, on continued treatment, loses a second molecule of ammonia and passes into the same Nt_2 -4-hydroxynaphthindone as is formed from naphthyl blue and violet.

Magdala red itself is obtained when amidoazonaphthalene is heated with phenol at 130°, and, on treatment with hydrochloric acid, yields the corresponding indones, $\text{C}_{30}\text{H}_{19}\text{N}_3\text{O}$ and $\text{C}_{30}\text{H}_{18}\text{N}_3\text{O}_2$. The second of

these dissolves in alkalis, forming red solutions which have a fiery fluorescence. The constitution of Magdala red is therefore



which also shows its relation to naphthyl red.

The details of the investigation will be subsequently published.

A. H.

Phenanthridone. By A. PICTET and E. PATRY (*Ber.*, **26**, 1962—1968).—In order to explain the difference between Pictet and Ankersmit's so-called hydroxyphenanthridine (*Abstr.* 1892, 196) and Graebe and Wander's phenanthridone (this vol., i, 658), the authors were led to study the oxidation of phenanthridine. This base, however, withstands the action of most oxidising agents, but ultimately the following method was adopted. The finely-pulverised phenanthridine (1 gram) was mixed with a 20 per cent. solution of bleaching powder (500 c.c.) and a 10 per cent. solution of cobalt nitrate dropped into the boiling liquid until the reaction ceased, after which the boiling was continued for an hour. The liquid, when cold, was filtered, and the oxidation product isolated from the cobalt oxide by extraction with hot alcohol or, preferably, by sublimation. In this way a compound was obtained melting at 293° (corr.) identical with Graebe and Wander's phenanthridone, so that the nature of Pictet and Ankersmit's compound still remains an open question. Acridine is more advantageously converted into acridone by the method just described than by that of Graebe and Lagodzinski (this vol., i, 649). Pictet and Ankersmit have already shown that when phenanthridine methiodide is treated with alkali, it is converted into a methyl hydroxide. When the latter is oxidised with alkaline ferricyanide solution, *methylphenanthridone*, $\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{CO} \\ | \\ \text{C}_6\text{H}_4\cdot\text{NMe} \end{array}$, is obtained; this crystallises from alcohol in white needles, melts at 108°, and is insoluble in water, dilute acids, and alkalis.

Phenanthridine ethiodide is obtained by heating phenanthridine with ethylic iodide in a sealed tube at 100°; it melts at 253°, and yields the *ethyl hydroxide* melting at 95° when treated with alkalis. By oxidising the latter with alkaline ferricyanide, *ethylphenanthridone*, $\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{CO} \\ | \\ \text{C}_6\text{H}_4\cdot\text{NEt} \end{array}$, melting at 88°, is formed.

Benzylphenanthridone, $\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{CO} \\ | \\ \text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CH}_2\text{Ph} \end{array}$, is obtained by heating phenanthridine with benzylic chloride, treating the *phenanthridine benzyl chloride* so prepared with alkali, and oxidising the resulting *hydroxide* with alkaline ferricyanide; it forms small, white leaflets, and melts at 115°.

A. R. I.

Orientation in the Terpene Series. By A. BAEYER (*Ber.*, **26**, 2267—2271; this vol., i, 359).—A *tertiary menthol* is obtained by treating menthene with a solution of hydrogen iodide or bromide in acetic acid cooled with ice, and then decomposing the pure halogen

derivative dissolved in acetic acid with silver acetate. The *acetate* obtained in this way is separated from menthene by distillation in a vacuum and hydrolysed. The alcohol boils at 97—101° under 20 mm. pressure, has a faint odour of peppermint, and solidifies to a vitreous mass when cooled with solid carbonic anhydride. It behaves as a tertiary alcohol towards chromic acid and halogen hydrides. The *bromide* prepared from it, when heated with quinoline, yields menthene (b. p. 167·5°).

Tertiary carvomenthol, obtained from carvomenthene in a similar way, boils at 96—100° under 17 mm. pressure, is similar to the tertiary menthol, and when its bromide is heated with quinoline yields carvomenthene (b. p. 174·5°).

Tertiary menthylamine is obtained by treating the tertiary iodide or bromide obtained from menthene in ethereal solution with silver cyanate and hydrolysing the oil thus produced with alkali. The *hydrochloride* melts at 205°. The *platinochloride* crystallises in leaflets, and decomposes at 235°. The *phenylthiocarbamide* crystallises in radiating leaflets, and melts at 118—119°. The *benzoyl compound* crystallises in needles, and melts at 154·5°.

Tertiary carvomenthylamine is obtained in a similar way. The *hydrochloride* is a syrup which slowly crystallises. The *phenylthiocarbamide* crystallises in prisms, and melts at 128°. The *benzoyl compound* crystallises in large needles and melts at 110°. E. C. R.

Carvole. By H. GOLDSCHMIDT (*Ber.*, 26, 2084—2087).— γ -Carvoxime, on reduction with sodium amalgam, or zinc dust and acetic acid, yields carvylamine, $C_{10}H_{17}N$, not the dihydrogen derivative as assumed by Wallach (*Abstr.*, 1892, 499); the previous observations of Goldschmidt and Kisser are, therefore, confirmed. The amine boils at 98—99° under a pressure of 10 mm., and consists of two stereoisomerides which can be separated by the fractional crystallisation of their benzoyl derivatives. The α -modification, $C_{10}H_{16}NBz$, is sparingly soluble in benzene, and crystallises in long, slender, colourless needles, melting at 168—169°. The corresponding α -carvylphenylcarbamide, $C_{10}H_{15}\cdot NH\cdot CO\cdot NHPh$, melts at 187—191°, and could not be completely freed from the β -derivative. β -Carvylamine nitrate is less soluble than the corresponding α -salt; the benzoyl derivative, $C_{10}H_{15}\cdot NHBz$, crystallises in long, transparent plates, melting at 103°. β -Carvylphenylcarbamide is deposited in small, colourless needles, melting at 138°. The formula $C_{10}H_{15}NO$ for isocarvoxime (m. p. 143—144°) is confirmed, its molecular weight having been determined by means of the boiling point method, using ether as solvent; it is optically inactive, and by the action of dilute sulphuric acid is resolved into hydroxylamine, carvacrolé, and carvoline. The carvacrole was identified by means of the phenyl cyanate derivative, which is deposited from light petroleum in long, transparent needles, melting at 134—135°. Carvoline, which is isomeric with carvacol, melts at 94°, and is probably a secondary base.

Carvacrylamine, $NH_2\cdot C_6H_3Me, Pr^a [= 1 : 2 : 5]$, is formed by the reduction of isocarvoxime in alcoholic solution with zinc dust and acetic acid, and is identical with the compound obtained by the action of zinc ammonium chloride on carvacrole: the acetyl derivative melts at

71°, and not at 115°, as stated by Lloyd. The yield of carvacrylamine was 44 per cent. of the theoretical. By the reduction of isocarvoxime with zinc dust in glacial acetic acid solution, carvacrylamine and carvoline are obtained; the latter is probably derived from the former by rearrangement (Beckmann's reaction). Isocarvoxime on reduction with sodium and alcohol, yields carvacrylamine, carvoline, and a hydrogenised base which is being further investigated. J. B. T.

Isomeric Menthylamines. By O. WALLACH and M. KUTHE (*Annalen*, **276**, 296—314).—Representing menthone by the formula $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} \text{CH} \cdot \text{C}_3\text{H}_7$, it is seen to contain two asymmetrical carbon atoms. When the carbonyl group is converted into the group $\text{CH} \cdot \text{NH}_2$, a third carbon atom is rendered asymmetrical, and the production of optical isomerides becomes possible. Now, it has been previously shown (*Ber.*, **25**, 3313) that by reducing *l*-menthone-oxime (see also Andres and Andreef, *Abstr.*, 1892, 723), a *lævo*-rotatory menthylamine is formed, whilst the base prepared from menthone and ammonium formate consists mainly of a *dextro*-rotatory compound together with some of the *lævo*-rotatory isomeride. That these two isomerides do not rotate the plane of polarised light in opposite directions to an equal extent is what might be expected, for if the optical function of the two asymmetrical carbon atoms in *l*-menthone experiences no alteration by the appearance of a third, the two isomeric menthylamines which might theoretically be formed cannot possibly have equal rotatory powers in opposite directions. The two isomerides are distinguished as *l*- and *r*-menthylamine, and inasmuch as they exhibit many analogies with the hydrogenised phthalic acids, they may be regarded as *cis*- and *trans*-forms respectively.

A yield of *l*-menthylamine, $\text{C}_{10}\text{H}_{19}\text{NH}_2$, amounting to 90 per cent. of the theoretical is obtained when *lævo*menthone is dissolved in absolute alcohol, and the solution boiled with sodium; it boils constantly at 205°. The *hydrochloride* is a snow-white powder which does not melt at 280°, and the *hydrobromide* crystallises in needles and becomes brown at 200°. The *formyl* derivative, $\text{C}_{10}\text{H}_{19}\text{NH} \cdot \text{COH}$, melts at 102—103°; the *acetyl* derivative melts at 145°, the *propionyl* derivative at 89°, and the *butyryl* derivative at 80°. *l*-Phenylmenthylthiocarbamide, $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_{19}$, is prepared by treating an ethereal solution of *l*-menthylamine with phenylthiocarbimide; it forms lustrous crystals, and melts at 135°. *l*-Benzylidenementhylamine, $\text{C}_{10}\text{H}_{19}\text{N} : \text{CHPh}$, is obtained by treating a methyl alcoholic solution of *l*-menthylamine with benzaldehyde; it melts at 69—70°. The *ortho*-hydroxybenzylidene derivative melts at 56—57°.

When *lævo*menthone is heated with ammonium formate at 190—200°, the product is a mixture of *r*- and *l*-formylmenthylamine. *r*-Menthylamine is obtained by boiling the formyl derivative with alcoholic potash; it has the same boiling point as *l*-menthylamine, but the derivatives of the two differ in melting point and solubility (see also above). The *hydrochloride* crystallises in tables, and melts at 189°; the *hydrobromide* melts at 225°; and the *hydriodide* melts at 270° with decomposition. *r*-Formylmenthylamine, $\text{C}_{10}\text{H}_{19}\text{NH} \cdot \text{COH}$,

melts at 117.5° ; the *acetyl* derivative, $C_{10}H_{19}\cdot NHAc$, melts at $168-169^{\circ}$, the *propionyl* derivative at 151° , and the *butyryl* derivative at $105-106^{\circ}$.

r-Phenylmenthylthiocarbamide, $NHPh\cdot CS\cdot NHC_{10}H_{19}$, melts at $178-179^{\circ}$; *r*-allylmenthylthiocarbamide, $C_3H_5\cdot NH\cdot CS\cdot NH\cdot C_{10}H_{19}$, melts at 110° ; *r*-benzylidenementhylamine crystallises in lustrous needles, and melts at $42-43^{\circ}$; its *orthohydroxy*-derivative melts at $96-97^{\circ}$.

The author finds that when *lævomenthone* is treated with concentrated sulphuric acid in the manner described by Beckmann (Abstr., 1889, 722), a certain amount is converted into *dextromenthone*.

A. R. L.

Optical Rotatory Powers of certain Compounds of the Fenchylamine and Menthylamine Series. By O. WALLACH and A. BINZ (*Annalen*, 276, 315-327).—The following table contains the mean values obtained for the specific and molecular rotatory powers of fenchone and its derivatives in chloroform solutions.

	Melting point.	$[\alpha]_D$.	$[M]_D$.
Fenchonoxime	165.0°	$+52.44^{\circ}$	$+87.46^{\circ}$
Fenchylamine	—	-24.89	-38.00
Formylfenchylamine	114.0	-36.56	-66.04
Acetylfenchylamine	99.0	-46.62	-90.73
Propionylfenchylamine	123.0	-53.16	-110.88
Butyrylfenchylamine	77.5	-53.11	-118.19
Benzylidenefenchylamine	42.0	$+73.14$	$+175.90$
Orthohydroxybenzylidenefenchylamine.	94.0	$+66.59$	$+170.77$
Parahydroxybenzylidenefenchylamine..	175.0	$+72.00$	$+184.65$
Orthomethoxybenzylidenefenchylamine	56.0	$+59.20$	$+160.09$
Paramethoxybenzylidenefenchylamine .	55.0	$+78.05$	$+211.07$

The values for the rotatory powers of the *ortho*- and *para*-hydroxybenzylidene derivatives show that the alteration in the rotatory power of active substances by the introduction of a radicle is not, as Guye supposes (*Arch. Sci. phys. nat.*, 1891, 97), a function of the molecular weight of that radicle.

The optical investigation of derivatives of *l*- and *r*-menthylamine

	$[\alpha]_D$.	Diff.	$[M]_D$.	Diff.
<i>l</i> -Formylmenthylamine	-83.37°		-152.27°	
<i>l</i> -Acetylmenthylamine	-81.81	1.56	-160.84	8.57
<i>l</i> -Propionylmenthylamine	-76.53	5.28	-161.15	0.31
<i>l</i> -Butyrylmenthylamine	-72.10	4.43	-160.90	0.75
<i>r</i> -Formylmenthylamine	$+54.03$		$+98.68$	
<i>r</i> -Acetylmenthylamine	$+50.57$	3.46	$+99.42$	0.74
<i>r</i> -Propionylmenthylamine	$+45.14$	5.43	$+95.05$	4.37
<i>r</i> -Butyrylmenthylamine	$+40.59$	4.55	$+91.14$	3.91

(last abstract) seemed particularly adapted to elucidate the question whether analogous compounds having common differences exhibit any regularity in the alteration of their rotatory powers. It is seen by the preceding table (p. 725) that this is not the case. The compounds were examined in chloroform solutions.

A somewhat striking regularity is exhibited by comparing the similar derivatives of the two series, thus.

	[α] _D .	Diff.
l.-Formylmenthylamine	-83.37°	} 29.34
r.-Formylmenthylamine	+54.03	
l.-Acetylmenthylamine	-81.81	} 31.24
r.-Acetylmenthylamine	+50.57	
l.-Propionylmenthylamine	-76.53	} 31.39
r.-Propionylmenthylamine	+45.14	
l.-Butyrylmenthylamine	-72.10	} 31.51
r.-Butyrylmenthylamine	+40.59	

A. R. L.

Essence of Eucalyptus globulus. By E. SPIZZICHINO (*L'Orosi*, 16, 1—6).—50 kilos. of the dried leaves of *Eucalyptus globulus* yield on distillation about 600 grams of oil. On prolonged boiling with alcoholic soda, the essence loses its characteristic odour, and acquires that of camphor, whilst the soda solution probably retains acetic and valeric acids, resulting from the hydrolysis of some constituents of the essence. The oil, purified by this means, boils principally at 170—180°; the fraction boiling at 170—175°, when treated with barium oxide and fractionated, gives pure eucalyptol, $C_{10}H_{18}O$, boiling at 171—173°. It has a camphor-like odour, does not react with phenylhydrazine or hydroxylamine, and is but slightly acted on by sodium.

On heating a mixture of eucalyptol and metanitrobenzaldehyde in molecular proportion with a little dilute sulphuric acid, vigorous action occurs. The friable mass obtained on cooling, when purified by the method employed by Bertoni in similar cases (*Abstr.*, 1891, 1378), yields *metanitrophenoleucalyptolmethane*, $NO_2 \cdot C_6H_4 \cdot CH : C_{10}H_{16}O$, as a reddish, amorphous powder; it is soluble in chloroform, acetone, ethylic acetate, and benzene, but insoluble in water or light petroleum. On heating, it softens and explodes slightly with evolution of yellow vapours.

W. J. P.

Essence of Eucalyptus. By G. BOUCHARDAT and OLIVIERO (*Bull. Soc. Chim.*, [3], 9, 429—432).—The essence of eucalyptus contains aldehydes—valeraldehyde with a little hexylaldehyde and, in some samples, butaldehyde; alcohols—mainly ethyl and amyl (mostly inactive) alcohols, eucalyptol, and a laevorotatory substance $C_{20}H_{36}$, together with a dextrorotatory substance of higher boiling point. The examination of the latter substances is proceeding.

W. T.

Essence of Niaouli. By G. BERTRAND (*Bull. Soc. Chim.*, [3], 9, 432—437).—The essence of niaouli contains:—(1), in small quantity, volatile fatty acids, especially valeric acid, a substance which may be methylic salicylate, a thio-compound, ethereal salts of terpenol, and benzaldehyde with a trace of valeraldehyde; (2) as principal constituents, a dextrorotatory turpentine, inactive eucalyptol boiling at 175° (forming two-thirds by weight of the essence), a lævoro-rotatory citrene boiling at 175° , and terpenol boiling at 218° .

W. T.

Anemonin and its Occurrence. By W. K. J. SCHOOR (*Chem. Centr.*, 1893, ii, 60; from *Maandbl. natuurw.*, 18, 23—40).—Anemonin occurs in many of the *Ranunculaceæ*; it is a toxic substance, and produces paralysis of the central nervous system. The compound has the formula $C_{15}H_{12}O_6$, and is deposited in rhombic crystals melting at 152° . It is volatile with steam, and on exposure to air at ordinary temperatures is slowly converted into anemonic acid; the oxidation proceeds more quickly if platinum black, hydrogen peroxide, or barium peroxide is employed.

J. B. T.

Crystalline Acid from Lichen (Thamnolic acid). By W. ZOFF (*Chem. Centr.*, 1893, ii, 54—55; from *Hedwigia*, 1893, 66—69).—The author has prepared, from *Thamnolia vermicularis*, a compound which he proposes to term *thamnolic acid*, to the presence of which the plant owes its light colour. The lichen is extracted with dilute soda, the solution acidified with hydrochloric acid, and the precipitate crystallised from methyl alcohol; it melts at $202\text{--}204^{\circ}$ with decomposition.

J. B. T.

Valency of Nitrogen in Pyrroline. By E. BAMBERGER (*Ber.*, 26, 1946—1947).—A reply to Ciamician and Zanetti (this vol., i, 602).

Amido- and Nitro-derivatives of Pyridine. By W. MARCKWALD (*Ber.*, 26, 2187—2189).—2-Chloropyridine will not exchange its chlorine for amidogen, but chloronicotinic acid [$Cl : COOH = 2 : 5$] does, when heated with strong aqueous ammonia at 170° . The product, *amidonicotinic acid* [$NH_2 : COOH = 2 : 5$], forms minute crystals which melt above 300° ; when heated, it loses carbonic anhydride, and yields 2-*amidopyridine*, which melts at 56° , and boils at 204° . When amidonicotinic acid is dissolved in strong sulphuric acid and the theoretical quantity of strong nitric acid added, *nitramidonicotinic acid* [$NO_2 : NH_2 : COOH = 3 : 2 : 5$ probably] is obtained; it forms small, yellow crystals which melt at about 280° .

C. F. B.

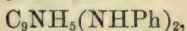
Amido-derivatives of Quinoline. III. By J. EPHRAIM (*Ber.*, 26, 2227—2230; compare *Abstr.*, 1891, 1509; 1892, 1493).— γ -Chloroquinaldine reacts with phenylhydrazine at 115° yielding *phenylhydrazo- γ -quinaldine*, $C_9H_5Me \cdot NH \cdot NHPh$, which forms yellowish white crystals melting at $134\text{--}135^{\circ}$. This substance has strongly

basic properties, and gives a *hydrochlorile* which melts at 272° with decomposition.

γ -*Amidoquinaldine* is obtained by the reduction of the foregoing compound, and forms beautiful white needles melting at 168° . The *platinchloride* of the base melts at 228° .

It has been shown that in the quinoline ring a chlorine atom in the α - or γ -position will react with bases, whilst if in the β -position no reaction takes place even on continued heating. This reaction may, therefore, be used as a means of ascertaining the constitution of halogen derivatives of quinoline. Thus, kynurenic acid may be converted by loss of carbonic anhydride into kynurin, from which a chloroquinoline can be prepared. This substance, when heated with aniline, enters into reaction, and yields a *phenylamidoquinoline* melting at 198° . The chloroquinoline, which is undoubtedly different from the α -compound, must therefore be γ -chloroquinoline, and the position of the hydroxyl group in kynurin and kynurenic acid is also thus determined.

γ -Chlorocarbostryl forms an exception to the general rule as stated above. In order to ascertain the reason of this exceptional behaviour, this substance was converted by the action of phosphorus pentachloride into $\alpha\gamma$ -dichloroquinoline, and the latter heated with aniline. A reaction takes place, and $\alpha\gamma$ -*dianilidoquinoline*,



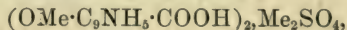
melting at 149° , is formed. α -Ethoxy- γ -chloroquinoline also reacts with aniline yielding α -ethoxy- γ -phenylamidoquinoline, which crystallises from alcohol in white needles, and does not melt below 270° .

The stability of the chlorine atom of γ -chlorocarbostryl towards bases seems, therefore, to be due to the presence of the hydroxyl group.

A. H.

Alkyl and Alkylene Derivatives of Substituted Cinchonic acids. By A. CLAUS (*Annalen*, **276**, 266—267).—General and introductory remarks on the papers following.

Alkyl Derivatives of Quininic acid. By A. CLAUS and F. STOHR (*Annalen*, **276**, 267—281).—When quininic acid is heated with an excess of methylic iodide in a sealed tube at 130° , the *methiodide*, $\text{OMe}\cdot\text{C}_9\text{NH}_5\cdot\text{COOH}\cdot\text{MeI}$, is obtained; it forms yellow, lustrous needles, melts at 205° with decomposition, and is soluble in boiling water and alcohol. The *methochloride* melts at 215° . The *sulphate*,

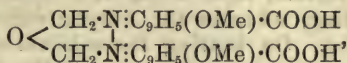


obtained by treating the methohalogen compounds with silver sulphate, melts at 245° ; and the nitrate, $\text{OMe}\cdot\text{C}_9\text{NH}_5\cdot\text{COOH}\cdot\text{MeNO}_3$, formed by treating them with silver nitrate, melts at 192° .

Quininicacid methylbetaïne, $\text{OMe}\cdot\text{C}_9\text{NH}_5\cdot\text{Me} < \begin{smallmatrix} \text{CO} \\ | \\ \text{C} \end{smallmatrix}$, is obtained by treating a cold aqueous solution of either of the last-described methohalogen compounds with moist silver oxide, or by treating the methosulphate with barium hydroxide; it crystallises in tufts of

yellow needles, melts at 194° with decomposition, and is readily soluble in water, but insoluble in ether; the salts formed by the action of acids are identical with those obtained from the methohalogen derivatives of quinic acid and silver salts.

Methyleneparamethoxycinchonic acid,



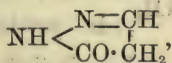
is formed by treating the metho-salts, above described, with moderately dilute potash, and adding a slight excess of dilute acid to the red solution; the precipitate, in the freshly precipitated, moist condition, is readily soluble in ether, but loses its solubility when dried; it is an intensely yellow powder, melts at 282° , has no basic properties, and is soluble in alcohol, but only very sparingly in water. The *silver* salt is a grey precipitate, and the *copper* salt is a dark green precipitate.

Quinic acid ethobromide, $\text{OMe}\cdot\text{C}_9\text{NH}_5\cdot\text{COOH}\cdot\text{EtBr}$, melts at 210° , and the *propobromide* at 192° . *Quinic acid benzylobromide*, $\text{OMe}\cdot\text{C}_9\text{NH}_5\cdot\text{COOH}\cdot\text{CH}_2\text{PhBr}$, is obtained by heating quinic acid and benzylic bromide in a sealed tube at 130° ; it crystallises from alcohol in yellow, lustrous needles, melts at 149° with decomposition, and is sparingly soluble in water, insoluble in ether, chloroform, and benzene. When treated with silver oxide, it gives the *benzyl-betaïne* $\text{C}_{18}\text{H}_{15}\text{NO}_3$; this crystallises in tufts of prisms having the colour of topaz, and melts at 159° . *Benzylideneparamethoxycinchonic acid*, $\text{O} < \begin{array}{c} \text{CHPhN:C}_9\text{H}_5(\text{OMe})\cdot\text{COOH} \\ \text{CHPhN:C}_9\text{H}_5(\text{OMe})\cdot\text{COOH} \end{array}$ is obtained by treating the benzyl-betaïne with moderately concentrated alkalis, and acidifying the solution; it crystallises from alcohol in lustrous, transparent needles, and melts at 270° ; the *silver* salt is a brownish-yellow powder, and the *copper* salt a bright green powder.

A. R. L.

Pyrazines and Piperazines. By L. WOLFF (*Ber.*, 25, 1923—1925).—A reply to Stoehr (this vol., i, 612), who has questioned the accuracy of certain data and opinions published by the author.

Derivatives of Pyrazolone. By R. v. ROTHENBURG (*Ber.*, 26, 2053—2059; compare *Abstr.*, 1893, i, 180).—*Pyrazolone*,



is less stable than its derivatives; on treatment with concentrated hydrochloric acid, a salt is first formed, but is rapidly decomposed into humus-like substances. Nitrous acid converts it into an *isonitroso-compound*, $\text{NH} < \begin{array}{c} \text{N}=\text{CH} \\ \text{CO}\cdot\text{C}\cdot\text{NOH} \end{array}$, which crystallises in reddish-yellow needles melting at 87° , and is decomposed by an excess of nitrous acid.

Pyrazolone-3-carboxylic acid, $\text{NH} \begin{smallmatrix} \text{N}=\text{C} \text{ COOH} \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$, is formed in very small quantity by the oxidation of 3-methylpyrazolone, as well as by the ordinary method of preparation (Abstr., 1893, i, 180). It forms crystalline salts of *sodium*, *ammonium*, and *copper*. The free acid decomposes on heating, whereas the ethylic salt may be distilled without decomposition. On heating the calcium salt, pyrazolone is formed, together with 3-dipyrzolononeketone, $\left(\begin{smallmatrix} \text{NH}-\text{N} \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix} \gg \text{C} \right)_2 \text{CO}$, which is a thick, yellow oil, is very sensitive to light, and boils at 203—204°. It reacts with phenylhydrazine acetate to form 3-dipyrzolonemethylenephénylhydrazone, $\left(\begin{smallmatrix} \text{NH}-\text{N} \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix} \gg \text{C} \right)_2 \text{C}:\text{N} \cdot \text{NHPh}$, which melts at 113°. *Methylic pyrazolonecarboxylate*, $\begin{smallmatrix} \text{NH}-\text{N} \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix} \gg \text{C}:\text{COOMe}$, may be prepared from methylic oxalacetate or methylic acetylenedicarboxylate by the action of hydrazine hydrate, or by the etherification of pyrazolonecarboxylic acid with methyl alcohol and hydrochloric acid; it forms yellow crystals melting at 226.5—227.5°. The *amide* is an indistinctly crystalline mass melting with decomposition at 219°.

Methylic 4-benzalpyrazolone-3-carboxylate, $\text{NH} \begin{smallmatrix} \text{N}=\text{C} \cdot \text{COOMe} \\ \text{CO} \cdot \text{C}:\text{CHPh} \end{smallmatrix}$, is a sparingly soluble powder melting above 250°.

Methylic 4-azobenzenepyrazolone-3-carboxylate, $\text{NH} \begin{smallmatrix} \text{N}=\text{C} \cdot \text{COOMe} \\ \text{CO} \cdot \text{C}:\text{N} \cdot \text{NHPh} \end{smallmatrix}$, which is prepared by the action of diazobenzene sulphate, crystallises from alcohol in fiery-red crystals melting at 209—211°, and has acid properties.

Methylic 4-isonitrosopyrazolone-3-carboxylate, $\text{NH} \begin{smallmatrix} \text{N}=\text{C} \cdot \text{COOMe} \\ \text{CO} \cdot \text{C}:\text{NOH} \end{smallmatrix}$, is prepared by the action of nitrous fumes on an alcoholic solution of the methylic salt. It crystallises in yellowish-red granules, melts at 199—201°, and is a strong acid. It forms deep-red solutions with alkalis, and yields a red, granular *silver salt*, which detonates when rapidly heated. When its alcoholic solution is treated with hydrazine hydrate, 4-hydrazipyrazolone-3-carbonylhydrazine, $\text{NH} \begin{smallmatrix} \text{N}=\text{C} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2 \\ \text{CO} \cdot \text{C}:\text{N} \cdot \text{NH}_2 \end{smallmatrix}$, is produced; this melts above 250°, and loses hydrazine when boiled with acids or alkalis. On treatment with benzaldehyde, it yields 4-benzalazipyrazolone-3-carbonylbenzalhydrazine, $\text{NH} \begin{smallmatrix} \text{N}=\text{C} \cdot \text{CO} \cdot \text{NH} \cdot \text{N}:\text{CHPh} \\ \text{CO} \cdot \text{C}:\text{N} \cdot \text{N}:\text{CHPh} \end{smallmatrix}$, which forms yellow needles melting at 217.5°.

When 4-isonitrosopyrazolone-3-carboxylic acid is treated with excess of hydrazine hydrate, the *lactam* of 4-hydrazipyrazolonecarboxylic acid, $\text{NH} \begin{smallmatrix} \text{N}=\text{C} \cdot \text{CO} \\ \text{CO} \cdot \text{C}=\text{N} \end{smallmatrix} \text{NH}$, is produced. This compound

crystallises from dilute hydrochloric acid in white granules, decomposing at 125—126°; it does not give a benzal compound on treatment with benzaldehyde, or yield hydrazine on boiling with alkalis or acids. It probably exists in the lactim form in its intensely coloured, reddish-yellow alkaline solution.

Attempts to prepare derivatives of pyrazolone by the action of hydrazine hydrate on ethylic anilidoacrylate and ethylic cinnamate, by the abstraction of water from tartrylhydrazine, and by the action of ammonia on phenyloxazolone, proved unsuccessful. Phenyloxazolone

was, however, converted into 3-phenylpyrazolone, $\text{NH}-\text{N} \begin{smallmatrix} \diagup \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix} \text{CPh}$, by the action of hydrazine hydrate.

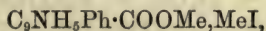
Tartrylhydrazine, $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, is slightly soluble in alcohol, readily in water, and forms delicate, matted needles melting at 182.5—183°. *Tartrylbenzalhydrazine*, $\text{C}_2\text{H}_5(\text{OH})_2\cdot(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh})_2$, forms yellowish plates, and melts at 225°. A. H.

Alkyl Derivatives of 2'-Phenylcinchoninic acid. By A. CLAUS and B. BÜTTNER (*Annalen*, 276, 282—295).—2'-Phenylcinchoninic acid

methiodide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{COOH})\cdot\text{CH} \\ \diagdown \text{N}(\text{MeI}) \end{smallmatrix} \text{CPh}$, is obtained by heating cinchoninic acid with methylic iodide in a sealed tube at 130°. It crystallises from alcohol in lustrous, copper-coloured scales, and separates, on the addition of ether to the alcoholic solution, in orange-red needles; it melts at 182—186° with decomposition. The methochloride forms yellowish prisms, becomes green below 140°, and melts at 209—210° with decomposition. The methosulphate crystallises in rhombic prisms.

2'-Phenylcinchoninic acid methylbettaïne, $\text{C}_9\text{NH}_5\text{MePh} \begin{smallmatrix} \text{CO} \\ \diagdown \text{O} \end{smallmatrix}$, is formed when moist silver oxide is added to an aqueous alcoholic solution of the methiodide; it separates from its alcoholic solution in large, yellow, rhombic tables, becomes green at 100°, and melts at 220—221° with decomposition. The salts obtained on treating the methylbettaïne with acids are identical with those formed by the action of silver salts on 2'-phenylcinchoninic acid methiodide.

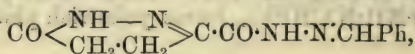
The methylbettaïne combines with methylic iodide when heated with it in a sealed tube at 100°, forming a methiodide,



which crystallises from water in small, garnet-red needles, and melts at 160—161° with decomposition. When the methylbettaïne is dissolved in alkali and the solution cautiously acidified with hydrochloric acid, 2'-phenylcinchoninic acid methochloride is obtained, but if the alkaline solution is evaporated, the residue redissolved in water, and the solution acidified with hydrochloric acid, a dark-coloured oxidation product is obtained. Further experiments are in progress.

A. R. L.

Pyridazolone. By R. v. ROTHENBURG (*Ber.*, **26**, 2061—2064).—Ethylic succinoformate, $\text{COOEt}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOEt}$, reacts with hydrazine hydrate in a similar manner to ethylic oxalacetate (*Abstr.*, 1893, i, 180), the product being *ethylic pyridazolone-3-carboxylate*, $\text{CO}\langle\text{NH}-\text{N}\rangle\text{C}\cdot\text{COOEt}$. This substance dissolves very readily in all solvents, and crystallises with difficulty in granules melting at $171.5-172^\circ$. It yields precipitates with silver nitrate and copper sulphate solutions, and does not react with nitrous acid or the salts of diazobenzene to form nitroso- or azo-compounds. On heating with hydrazine hydrate, it is converted into *pyridazolone-3-carbonylhydrazine*, $\text{CO}\langle\text{NH}-\text{N}\rangle\text{C}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, which forms very soluble granular crystals melting at 250° . On treatment with benzaldehyde, the carbonylhydrazine yields *pyridazolone-3-carbonylbenzylhydrazine*,



which separates from alcohol in white flakes melting above 250° .

Ethylic pyridazolonecarboxylate is rapidly decomposed by acids into hydrazine and succinoformic acid, but if alkalis are employed a small quantity of the free *pyridazolone-3-carboxylic acid* is also formed. This is only slightly soluble in water, and forms an indistinctly crystalline mass melting with decomposition above 250° . It yields an amorphous *silver salt*, and a crystalline *calcium salt*. When the latter is distilled with soda lime, a brown oil is produced, consisting of impure pyridazolone, $\text{CO}\langle\text{NH}-\text{N}\rangle\text{CH}$. This substance has not yet been obtained quite pure; it boils at $165-172^\circ$, and has an intense odour resembling those of pyridine and pyrazolone. Acids and alkalis decompose it with formation of hydrazine.

A. H.

Phthalazine. By S. GABRIEL and G. PINKUS (*Ber.*, **26**, 2210—2216).—*Phthalazine*, $\text{C}_6\text{H}_4\langle\text{CH}\rangle\text{N}_2$, may be prepared by heating tetrachlorortho-xylene, $\text{C}_6\text{H}_4(\text{CHCl}_2)_2$, with aqueous hydrazine at 150° , or, better, by converting it into phthalaldehyde and hydrochloric acid by boiling with water, and then adding potash and hydrazine sulphate, and concentrating, so as to complete the reaction $\text{C}_6\text{H}_4(\text{CHO})_2 + 4\text{HCl} + 5\text{KOH} + \text{N}_2\text{N}_4\text{H}_2\text{SO}_4 = \text{C}_6\text{H}_4\text{N}_2\cdot\text{HCl} + 3\text{KCl} + \text{K}_2\text{SO}_4 + 7\text{H}_2\text{O}$. It crystallises in yellowish needles, melts at $90-91^\circ$, and boils with partial decomposition at $315-317^\circ$; the *hydrochloride* forms needles melting at 231° with decomposition, the *platinochloride* brownish-yellow needles melting above 260° , and the *picrate* a crystalline precipitate melting at $208-210^\circ$. When phthalazine is reduced with zinc and hydrochloric acid, the nitrogen ring is broken, and orthoxylylenediamine, $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{NH}_2)_2$, is formed (compare Strassman, *Abstr.*, 1888, 474. Orthoxylylenediphthalimide and dibenzoylortho-xilylenediamine melt at $265-266^\circ$

and 184° respectively, not at 253° and 168°). *Diphenylsulphoneortho-xylylenediamine*, $C_6H_4(CH_2 \cdot NH \cdot SO_2Ph)_2$, prepared from the diamine, benzene sulphochloride, and soda, forms colourless plates melting at 127° . *Ortho-xylylenediamine* was also converted into the imine (dihydroisindole) by heating its hydrochloride. When phthalazine hydrochloride is reduced with sodium amalgam, the nitrogen ring remains intact, and *tetrahydrophthalazine*, $C_6H_4 \begin{smallmatrix} CH_2 \cdot NH \\ | \\ CH_2 \cdot NH \end{smallmatrix}$, is formed.

This is an unstable oil with reducing properties; its *hydrochloride* $C_8H_{10}HCl$ forms long, silky needles melting at 231° with decomposition; the *picrate* melts with decomposition at $159-160^{\circ}$; the *di-benzoyl derivative* forms needles which melt at $207-208^{\circ}$. The action of nitrous acid on the tetrahydro-compound yields an unstable (? dinitroso-) derivative, which decomposes in ethylic acetate solution, evolving nitrogen and forming a substance, $C_8H_8N_2O_2$, ? phthaldialdoxime, $C_6H_4(CH:NOH)_2$. This crystallises in lustrous, colourless prisms, and is not very stable; when treated with methylic iodide and sodium methoxide, it yields a colourless, crystalline substance, $C_8H_8N_2O$ (? $CN \cdot C_6H_4 \cdot CH \cdot NOME$), melting at $62-63^{\circ}$.

C. F. B.

Phenazones. By L. MEYER, Jun. (*Ber.*, 26, 2238-2242).—*Orthodinitrodityl*, obtained by the nitration of orthotolidine, behaves towards reducing agents in a similar manner to orthodinitrodiphenyl (Täuber, *Abstr.*, 1892, 183), phenazone derivatives being produced.

Ditolyleneazone or *tolazone*, $\begin{smallmatrix} N-C_6H_3Me \\ || \\ N-C_6H_3Me \end{smallmatrix}$ [$N_2 : Me_2 = 6 : 6' : 3' : 3$], is formed by the action of sodium amalgam on an alcoholic solution of dinitrodityl. It crystallises from alcohol in lustrous, yellow prisms, melts at 187° to a greenish-yellow liquid, and boils above 360° almost without decomposition. It is insoluble in water, readily soluble in alcohol, and very readily in benzene. It dissolves in acids with formation of unstable salts; the *hydrochloride* forms dark brown crystals, and the *platinochloride* is only slightly soluble in water. *Tolazone dioxide*, $C_{14}H_{12}N_2O_2$, is formed, along with a small amount of the monoxide, when dinitrodityl is reduced by means of potash and zinc dust. It crystallises in lustrous, straw-yellow plates, which melt at 128° with decomposition.

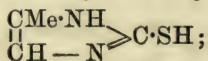
Diamidotolazone, $\begin{smallmatrix} N-C_6H_2Me \cdot NH_2 \\ || \\ N-C_6H_2Me \cdot NH_2 \end{smallmatrix}$ [$(NH_2)_2 = 4 : 4'$], is formed by the reduction of metadinitrorthotolidine by means of sodium amalgam. It forms dark red crystals melting with decomposition at 276° . It is readily soluble in alcohol, less readily in ether and benzene. The base is capable of forming several series of salts; thus, when it is dissolved in the smallest possible amount of hydrochloric acid, an olive-coloured solution is obtained, which, on the addition of more acid, changes to red.

Diamidotolazone reacts with benzaldehyde to form a *benzylidene* compound, $C_{28}H_{22}N_4$, which is obtained in yellow, lustrous crystals melting with decomposition at 239° .

Methylphenazonecarboxylic acid, $\begin{array}{c} \text{N}-\text{C}_6\text{H}_3\cdot\text{COOH} \\ || \\ \text{N}-\text{C}_6\text{H}_3\text{Me} \end{array}$, is obtained by the oxidation of tolazone with chromic acid. It forms light yellow needles, which undergo no alteration at 290°. The salts of the alkali metals are soluble in water, whilst those of zinc and cadmium are only very slightly soluble.

Attempts to prepare phenazonedicarboxylic acid have hitherto proved unsuccessful. A. H.

Amidoketones. By S. GABRIEL and G. PINKUS (*Ber.*, 26, 2197—2209).—*Amidoacetone*, $\text{COMe}\cdot\text{CH}_2\cdot\text{NH}_2$, may be prepared by boiling acetonylphthalimide, $\text{COMe}\cdot\text{CH}_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{O}_2$, with 20 per cent. hydrochloric acid, or, better, by reducing isonitrosoacetone, $\text{COMe}\cdot\text{CH}\cdot\text{NOH}$, in acid solution by means of stannous chloride, tin, and hydrochloric acid, or by zinc and acetic acid. The base itself cannot be obtained pure; it reduces Fehling's solution in the cold. The *hydrochloride* forms a fibrous, deliquescent, crystalline mass; the *platinochloride*, $(\text{C}_3\text{H}_7\text{NO})_2\cdot\text{H}_2\text{PtCl}_6$, yellow needles which melt with decomposition at 188—189°; and the *sodium picrate*, $\text{C}_3\text{H}_7\text{NO}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7\cdot\text{C}_6\text{H}_2\text{N}_3\text{O}_7\cdot\text{Na} + \text{H}_2\text{O}$, short prisms melting at 171—173°. The hydrochloride, when treated with phenylhydrazine and sodium acetate at 50°, yields methylphenylglyoxalosazone, $\text{N}_2\text{HPh}\cdot\text{COMe}\cdot\text{CH}\cdot\text{N}_2\text{HPh}$ (Japp and Klingemann, *Trans.*, 1888, 531). With potassium thiocyanate on the water bath, it yields *methylimidazolyl-μ-mercaptan*,



this crystallises in yellowish needles, melts at 242—245°, and is oxidised by hot 10 per cent. nitric acid to *methylimidazole*, $\begin{array}{c} \text{CMe}\cdot\text{NH} \\ || \\ \text{CH}-\text{N} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{CH}$,

which is an oil boiling at 263° under 764 mm. pressure; it yields a *nitrate* $\text{C}_4\text{H}_6\text{N}_2\cdot\text{HNO}_3$, as colourless crystals melting with decomposition at 110°, and an *aurchloride*, $\text{C}_4\text{H}_6\text{N}_2\cdot\text{HAuCl}_4$, as yellow prisms melting at 200—201°. When a solution of amidoacetone hydrochloride, obtained by adding isonitrosoacetone to a solution of stannous chloride in strong hydrochloric acid, is successively treated with caustic potash and mercuric chloride, metallic mercury is deposited,

and the base is oxidised to *dimethylpyrazine*, $\text{N} \begin{array}{c} \text{CMe}\cdot\text{CH} \\ \diagdown \quad \diagup \\ \text{CH}\cdot\text{CMe} \end{array} \text{N}$ (compare *Abstr.*, 1892, 507). Amidoaldehyde, when treated with potash and mercuric chloride, is converted in an analogous manner into pyrazine itself (compare this vol., i, 373).

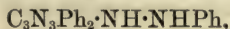
Amidopropyl methyl ketone, $\text{COMe}\cdot\text{CHEt}\cdot\text{NH}_2$, is obtained by reducing isonitrosopropyl methyl ketone with stannous chloride; the *hydrochloride* forms white needles, and melts at 150—151°; the *platinochloride* is a yellow, crystalline powder melting with decomposition at 184°. The base itself is obtained on adding potash to a strong solution of the hydrochloride; it is an oil which quickly solidifies to white crystals. C. F. B.

Pyrimidines Free from Oxygen. By A. PINNER (*Ber.*, 26, 2122—2125).—*Phenyltetrahydropyrimidine*, $\text{CPh} \begin{smallmatrix} \text{N}-\text{CH}_2 \\ \text{NH}\cdot\text{CH}_2 \end{smallmatrix} > \text{CH}_2$, is prepared by the action of benzamidine on trimethylenic bromide in ether-alcoholic solution at 30—40°. The reaction requires several weeks for completion, and the yield is small, considerable quantities of benzanide and bromopropylbenzamidine being also formed. The pyrimidine decomposes on distillation even under reduced pressure, and, like its simple salts, is a viscid liquid. The *platinochloride*, $\text{C}_{10}\text{H}_{12}\text{N}_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in yellow prisms melting at 215° with decomposition. Attempts to obtain methylphenylpyrimidine by the action of benzamidine on formylacetone were unsuccessful; benzamidinoglycollic acid was the only product which could be isolated.

Acetylacetone readily undergoes condensation with amidines at ordinary temperatures in presence of potassium carbonate; the fatty pyrimidines are viscid liquids, and have not yet been further investigated. The following compounds are prepared by the action of the corresponding amidine on acetylacetone; they are all readily soluble in acids, alcohol, ether, and benzene. *Phenyltrimethylpyrimidine*, $\text{CPh} \begin{smallmatrix} \text{N}\cdot\text{CMe} \\ \text{N}\cdot\text{CMe} \end{smallmatrix} > \text{CH}$, crystallises in long needles melting at 83°, and boiling at 276°.

Paratolyldimethylpyrimidine, $\text{C}_6\text{H}_4\text{Me}\cdot\text{C} \begin{smallmatrix} \text{N}\cdot\text{CMe} \\ \text{N}\cdot\text{CMe} \end{smallmatrix} > \text{CH}$, is deposited in silky, lustrous needles; it melts at 128°, and boils at 294°. *Benzyl-dimethylpyrimidine*, $\text{CH}_2\text{Ph}\cdot\text{C} \begin{smallmatrix} \text{N}\cdot\text{CMe} \\ \text{N}\cdot\text{CMe} \end{smallmatrix} > \text{CH}$, forms long needles melting at 80°, and boiling at 274°. *β-Naphthyltrimethylpyrimidine*, $\text{C}_{10}\text{H}_7\cdot\text{C} \begin{smallmatrix} \text{N}\cdot\text{CMe} \\ \text{N}\cdot\text{CMe} \end{smallmatrix} > \text{CH}$, crystallises in colourless needles; it melts at 116—117°, and boils considerably above 360° without decomposition. *Furyldimethylpyrimidine*, $\text{C}_4\text{OH}_3\cdot\text{C} \begin{smallmatrix} \text{N}\cdot\text{CMe} \\ \text{N}\cdot\text{CMe} \end{smallmatrix} > \text{CH}$, is first obtained as an oil which crystallises after some time. It closely resembles the phenyl derivative, melts at 54°, and boils at 263°. J. B. T.

Derivatives of Kyanidine. By J. EPHRAIM (*Ber.*, 26, 2226—2227).—*Diphenylchlorokyanidine*, $\text{C}_3\text{N}_3\text{Ph}_2\text{Cl}$, is obtained by the action of phosphorus oxychloride on diphenylhydroxykyanidine. It forms white needles which melt at 138—139°. The halogen atom of this substance is easily replaced by bases. On treatment with phenylhydrazine at 110°, *diphenylphenylhydrazokyanidine*,



is formed; it crystallises in reddish-white needles, and melts at 140°. Aniline produces *diphenylanilidokyanidine*, $\text{C}_3\text{N}_3\text{Ph}_2\cdot\text{NHPh}$, which forms lustrous, white plates melting at 155°. Alcoholic ammonia acts in a similar manner, producing *diphenylamidokyanidine*, $\text{C}_3\text{N}_3\text{Ph}_2\cdot\text{NH}_2$, which crystallises in lustrous needles, and melts at 172°.

The halogen atom of diphenylchlorokyanidine, which is combined

with a carbon atom adjacent to a nitrogen atom in a ring containing 3 nitrogen atoms, can therefore be replaced by bases in the same way as the similarly combined halogen atom in rings containing 1 and 2 atoms of nitrogen.

A. H.

Constitution of Hypoxanthine and Adenine. By M. KRÜGER (*Ber.*, 26, 1914—1922).—From analogy with uric acid and xanthine, one of the following formulæ is deduced for hypoxanthine, $\text{NH}\cdot\text{CH}\cdot\text{C}\cdot\text{NH}$ $\begin{smallmatrix} \text{N} \\ \parallel \\ \text{CH}\cdot\text{N}-\text{C}=\text{N} \end{smallmatrix}$ $>\text{CO}$ or $\begin{smallmatrix} \text{N}-\text{CH}\cdot\text{C}\cdot\text{NH} \\ \parallel \\ \text{CH}\cdot\text{NH}-\text{C}=\text{N} \end{smallmatrix}$ $>\text{CO}$, that of adenine being obtained from these by replacing O by NH. Either of these two formulæ also explains the following facts, recently observed by the author. Bromohypoxanthine forms a tetrabromo-additive compound; and, when oxidised with hydrochloric acid and potassium chlorate, yields carbamide and mesoxalylcarbamide. Dimethylhypoxanthine represents the maximum of substitution (of methyl for hydrogen), and, when hydrolysed with dilute sulphuric acid, yields methylamine and methylamidoacetic acid.

Bromohypoxanthine, $\text{C}_5\text{H}_3\text{BrN}_4\text{O}$, is obtained by treating bromadenine with nitrous acid. It crystallises with $2\text{H}_2\text{O}$ as a powder, with $1\frac{1}{2}\text{H}_2\text{O}$ in tufts of small needles; it may also be prepared by heating dry hypoxanthine with dry bromine at 120° ; the immediate product is in this case $\text{C}_5\text{H}_3\text{N}_4\text{OBr}\cdot\text{HBr}\cdot\text{Br}_2$. The sodium derivative, $\text{C}_5\text{H}_2\text{BrN}_4\text{ONa} + 2\text{H}_2\text{O}$, forms silky prisms. *Dimethylhypoxanthine*, obtained by heating hypoxanthine with sodium ethoxide, alcohol, water, and methylic iodide, crystallises in silky needles, and with sodium iodide forms a crystalline double salt, $\text{C}_7\text{H}_8\text{N}_4\text{O}\cdot\text{NaI} + 3\text{H}_2\text{O}$.

C. F. B.

Constitution of Nicotine. By A. PINNER (*Ber.*, 26, 2135—2137).—A reply to Étard (this vol., i, 675), who considers that the production of an acetyl derivative, which forms a platinochloride, proves the presence of an imide group in nicotine and establishes for it the formula $\text{CH}\cdot\text{CH}\cdot\text{C}-\text{CHEt}$ $\begin{smallmatrix} \parallel \\ \text{CH}\cdot\text{N}-\text{C}-\text{NH}\cdot\text{CH}_2 \end{smallmatrix}$ $>\text{CH}_2$. Working under similar condi-

tions to Étard, the author prepared, several years ago, a substance which appeared to be an additive compound of 1 mol. nicotine and 1 mol. acetic acid, but its homogeneity was open to doubt, and no conclusions can be drawn from its production. Blau has previously pointed out (*Abstr.*, 1891, 583) that if nicotine is represented by Étard's formula, it should yield, on oxidation, hydroxynicotinic acid or amidonicotinic acid, and not nicotinic acid.

J. B. T.

Benzoylnicotine. By A. ÉTARD (*Compt. rend.*, 117, 278—281).—When dry nicotine is mixed with excess of benzoic chloride, there is no action at the ordinary temperature, but if the mixture is heated intermittently to the boiling point of the benzoic chloride, there is an abundant evolution of hydrogen chloride, and benzoylnicotine is formed.

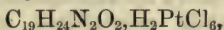
Benzoylnicotine is a colourless and somewhat viscous liquid, which

has no tendency to crystallise. It has a poisonous odour and a feeble taste, very different from that of nicotine, is insoluble in water, and dissolves only in a considerable excess of dilute hydrochloric acid. It is a feeble, monacid base, and the platinochloride is a pale yellow, crystalline compound, of the composition $(C_{10}H_{13}NBz)_2, H_2PtCl_6$.

It follows that, contrary to the general belief, acid chlorides do act on nicotine, and therefore the latter must contain hydrogen in direct union with nitrogen. This view is confirmed by the fact that, when anhydrous nicotine is heated at $160-170^\circ$ with dry aldehyde, it yields water and a viscous, insoluble base, with all the characteristics of the bases derived from aldehydes, which were discovered by Gerhardt and are commonly known as Schiff's bases.

The author considers that the cotinine and ticonine described by Pinner cannot contain the group NMe, but must contain secondary nitrogen, whilst the apocotinine and the compound $C_9H_{11}NO_4$, obtained from them respectively by reduction, must be regarded as pyridyl- β -butyric derivatives. C. H. B.

Transformation of Quinine. By Z. H. SKRAUP (*Monatsh.*, 14, 428—454).—This paper contains a detailed account of the researches formerly noticed in this vol., i, 56, and also the following additional facts. *Normal nichine sulphate*, $(C_{19}H_{24}N_2O_2)_2, H_2SO_4 + 10H_2O$, crystallises in needles; the *acid sulphate*, with $3\frac{1}{2}H_2O$, in colourless prisms; the *acid hydrochloride*, $C_{19}H_{24}N_2O_2, 2HCl$, in colourless prisms melting at about 234° ; the *acid hydriodide* in yellow prisms melting at $221-222^\circ$; the *acid oxalate* in aggregates of minute needles melting at 194° ; the *platinochloride* is yellow and amorphous. With hydriodic acid, nichine yields a *trihydriodide*, $C_{19}H_{24}N_2O_2, 3HI$, which melts with decomposition at 227° , and is converted by further heating with hydriodic acid into methylic iodide and the compound $C_{18}H_{22}N_2O_2, 3HI$, forming yellow needles melting at $219-220^\circ$; when heated with alcoholic potash, it is converted into *isonichine*, $C_{19}H_{24}N_2O_3$, which crystallises in white scales resembling benzoic acid, and melts at $208-209^\circ$; it yields a *trihydriodide*, and a *platinochloride*,



forming orange-red, crystalline aggregates.

With 3 mols. of ethylic iodide, nichine yields a crystalline additive compound, $C_{19}H_{24}N_2O_2, 2EtI + 2H_2O$, which melts at 137° ; with 1 mol., it yields, not an ethyl compound, but a *basic hydriodide*, $C_{19}H_{24}N_2O_2, HI$, which crystallises in white needles, and melts at $153-154^\circ$. With nitrous acid, nichine yields *nitroso-nichine nitrate*, $NO \cdot C_{19}H_{23}N_2O_2, HNO_3$, crystallising in yellow tables melting with decomposition at 172° , and from which alkalis liberate *nitroso-nichine* as a yellowish resin.

Pseudoquinine, $C_{20}H_{24}N_2O_2$, has a specific rotation $[\alpha]_D = -164.44^\circ$. The *normal nitrate*, $C_{20}H_{24}N_2O_2, HNO_3 + H_2O$, crystallises in prisms which melt at 130° , and again, after losing water, at 220° ; the *basic nitrate*, $(C_{20}H_{24}N_2O_2)_2, HNO_3 + 3H_2O$, in white needles melting at $175-177^\circ$; the *normal hydrochloride* ($1\frac{1}{2}H_2O$), in prisms melting at $256-257^\circ$; the *platinochloride*, $C_{20}H_{24}N_2O_2, H_2PtCl_6$, in minute plates. *Pseudoquinine*

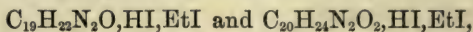
yields, with hydriodic acid, a *trihydriodide*, $C_{20}H_{24}N_2O_2 \cdot 3HI$, which seems to be identical with that obtained from quinine.

Potassium permanganate oxidises pseudoquinine and nichine with formation of substances analogous to the chitenine obtained from quinine, but whereas quinine yields, in addition, only formic acid, pseudoquinine yields but little formic acid and much acetic acid, and nichine little else but acetic acid. The same thing happens as regards these fatty acids, when chromic acid is used as the oxidising agent; in addition, quinine yields much, pseudoquinine little, and nichine very little, quininic acid.

C. F. B.

New Isomerides of the Ethiodides of the Cinchona Alkaloids.

By Z. H. SKRAUP and F. K. v. NORWALL (*Ber.*, 26, 1968—1970).—By heating the so-called neutral hydriodides of cinchonine, cinchonidine, and quinine with ethylic iodide, crystalline, yellow compounds are obtained of the respective composition



which, on being treated with ammonia, yield red, basic compounds, $C_{19}H_{22}N_2O \cdot EtI$ and $C_{20}H_{24}N_2O_2 \cdot EtI$; when the latter are heated with a fresh quantity of ethylic iodide, diethiodo-additive compounds are formed more readily than from the alkaloids themselves.

The new yellow salts are quaternary iodides, and it therefore follows that both the nitrogen atoms in the cinchona alkaloids are in tertiary combination. As the alkyl iodides of quinoline are yellow, the ethylic iodide of the new derivatives of the cinchona alkaloids must be in combination with the nitrogen of the quinoline nucleus.

A. R. L.

Allocinchonine. By E. LIPPMANN and F. FLEISSNER (*Ber.*, 26, 2005).—The base recently obtained by the authors from hydriodocinchonine dihydriodide (*Monatsh.*, May, 1893), and denominated by them pseudocinchonine, differs from a base described in the meantime by Hesse (this vol., i, 678) under the same name; they therefore propose to call their base *allocinchonine*. It melts at $214-216^\circ$, and may be identical with Hesse's apoisocinchonine (*loc. cit.*). However, allocinchonine dihydriodide crystallises with $1H_2O$, whereas the analogous salt of Hesse's apoisocinchonine is anhydrous; the platinum-chloride of the former is anhydrous, but that of the latter crystallises with $2H_2O$; the sulphates of the two bases also appear to differ.

A. R. L.

Dihydroxytropidine. By A. EINHORN and L. FISCHER (*Ber.*, 26, 2008).—*Dihydroxytropidine*, $CH \begin{array}{c} \text{NMe} \text{---} \text{CH}_2 \\ \diagup \text{CH(OH)} \cdot \text{CH(OH)} \diagdown \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array} CH$, is obtained

by dropping a solution of potassium permanganate into one of tropidine containing soda and cooled to 0° , driving over the unaltered tropidine from the filtrate with steam, and extracting with ether; it melts at 105° , and the *aurochloride* melts at 235° with decomposition.

A. R. L.

Melting Point of Cocaïne Hydrochloride. By O. HESSE (*Annalen*, 276, 342—344).—Kingel (*Pharm. Zeit.*, 38, 25) states

that cocaine hydrochloride melts at 200—202°, and that a lower melting point is indicative of impurities in the sample. The author finds that when the melting point of the pure salt is determined in a Roth's apparatus, or in a sulphuric acid bath, the temperature of which is raised slowly, the value 186° is obtained; whilst when a sulphuric acid bath is used and the temperature is raised rapidly, the salt melts at 200—202°.

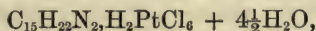
A. R. L.

Crystalline Form of Scopoline Platinochloride. By A. LADENBURG (*Annalen*, 276, 345—346).—An answer to Hesse (*Annalen*, 271, 100). The crystallographic measurements of pseudotropine platinochloride have been already given (Abstr., 1892, 1366). Scopoline platinochloride crystallises in the monosymmetric system, $a : b : c = 0.54108 : 1 : 0.5489$; $\beta = 119^\circ 45'$. The two bases are therefore distinct compounds.

A. R. L.

The Deliquescent Alkaloid from *Lupinus albus*. By A. SOLDAINI (*L'Orosi*, 16, 109—126).—The author has further examined the deliquescent alkaloid previously obtained by him from the seeds of *Lupinus albus* (this vol., i, 379). The alkaloid is not decomposed by boiling with 50 per cent. potash, but on heating it with caustic potash at 180°, a heavy, yellow oil with a coniine-like odour distils. This is strongly alkaline, and gives a crystalline, deliquescent hydrochloride which melts at 120°, and is soluble in alcohol; the aurochloride, $C_{15}H_{22}N_2 \cdot HAuCl_4$, forms small, yellow crystals melting at 193—194° with decomposition, and may be crystallised from boiling water without undergoing reduction. The aqueous solution of the residue in the retort gives up a small quantity of an alkaline oil on extraction with ether, and a platinochloride, $(C_7H_9N)_2 \cdot H_2PtCl_6 + H_2O$, may also be precipitated from it; this substance crystallises in yellow pyramids melting at 240° with decomposition.

On treating the hydrochloride of the original alkaloid with hydrochloric acid, dehydration occurs, and a deliquescent hydrochloride which melts at 154—155° is obtained; the platinochloride,



forms reddish pyramids which lose their water at 125—130°, and decompose at 210—212°. The alkaloid seems to contain no methoxyl group, as it does not give methylic chloride when heated in a sealed tube with hydrochloric acid; the action of phosphoric anhydride is similar to that of concentrated hydrochloric acid. No new products were obtained by heating the hydrochloride with soda-lime.

The alkaloid combines with 4 atoms of bromine in acetic acid solution, giving an unstable compound; this, by spontaneous loss of 1 mol. HBr, yields a substance containing 3 atoms of bromine; the latter, on crystallisation from boiling alcohol, decomposes, yielding the two following compounds. A hydrobromide, $C_8H_{13}NO \cdot HBr$, which forms very thin, white crystals melting at 224—225° with decomposition, and a hydrobromide melting at 134—135°. The former gives a red, crystalline aurochloride which decomposes at 140°, and deposits gold when its pure aqueous solution is boiled. The hydrobromide

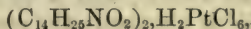
melting at $134-135^\circ$ yields a yellow, crystalline *platinochloride*, $(C_7H_5NO)_2, H_2PtCl_6 + 4\frac{1}{2}H_2O$, which decomposes at 210° ; the *hydrochloride* partially melts at $207-210^\circ$ with decomposition. The *aurochloride*, $(C_7H_5NO)_2, HAuCl_4$, is obtained as a yellow powder which softens at $120-122^\circ$.

The alkaloid is reduced by sodium in alcoholic solution, with production of a *hydrochloride* which forms small, soft crystals melting at $158-160^\circ$ with decomposition. The *aurochloride*, $C_{15}H_{30}N_2O, HAuCl_4$, forms small, yellow crystals which decompose at 145° with evolution of gas.

Phenylhydrazine and hydroxylamine seem to be without action on the alkaloid; the latter, however, reacts with potassium hydrogen sulphite, giving a product which is still under examination.

W. J. P.

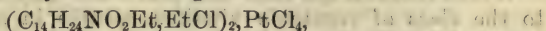
Carpaïne, the Alkaloid of the Leaves of Carica Papaya, L.
By J. J. L. VAN RYN (*Arch. Pharm.*, 231, 184-211).—The author gives an historical account of the papaw tree, a botanical description of its various parts, and mentions several methods for extracting the alkaloid from the dried leaves, of which Greshoff's (*Abstr.*, 1891, 334) gives the best results. Carpaïne crystallises in anhydrous, colourless, lustrous prisms melting at 121° , not at 115° as stated by Greshoff, and resolidifies at about 90° ; on further heating, it undergoes partial decomposition, some subliming in colourless needles. The alkaloid is extremely soluble in chloroform and carbon bisulphide, more sparingly in light petroleum and alcohol, and insoluble in water; in alcoholic solution it is dextrorotatory, $[\alpha]_D = +21.55^\circ$. The base does not give a colour reaction with sulphuric acid either alone or in presence of bromine water or vanadic anhydride; with potassium chromate and sulphuric acid, a green coloration is produced: nitric acid gives no reaction. The author's analyses of carpaïne agree closely with the formula $C_{14}H_{25}NO_2$; that assigned to it by Merck was $C_{14}H_{27}NO_2$. The *platinochloride*,



is yellow and crystalline; the *aurochloride* crystallises, with $5H_2O$, in lemon-yellow needles melting at 205° . The *hydrochloride* darkens at 225° , and decomposes at higher temperatures without melting. The *hydrobromide* is less soluble than the *hydrochloride*, and crystallises in colourless needles. The *hydriodide* resembles the *hydrochloride*, and crystallises in groups of pale yellow needles. The *hydrogen sulphate*, $C_{14}H_{25}NO_2, H_2SO_4 + 3H_2O$, is deposited in colourless, prismatic crystals on adding ether to its alcoholic solution. The *nitrate*, $C_{14}H_{25}NO_2, HNO_3 + H_2O$, forms prismatic, crystalline plates.

Ethylcarpaïne, $C_{14}H_{24}NO_2Et$, is prepared by the action of ethylic iodide on the alkaloid, and treatment of the product with potash; it crystallises from dilute alcohol in colourless, silky, lustrous needles melting at 91° . The compound is not affected by concentrated sulphuric acid or nitric acid, and does not react with Erdmann's reagent or Fröhde's reagent. The *hydriodide*, $C_{14}H_{24}NO_2Et, HI$, crystallises in slender needles melting at 235° , with partial decomposition. The *platinochloride* is a yellow, amorphous salt containing $3H_2O$. The

aurochloride crystallises in lemon-coloured needles melting at 175—176° with partial decomposition. By the action of ethylic iodide on ethylcarpaïne, *ethylcarpaïne ethiodide* is formed; it is crystalline and is not decomposed by soda. The *platinochloride*,



crystallises in yellow needles. The *aurochloride* forms lemon-coloured needles melting at 170—171°. It appears from the above results, that carpaïne is a secondary base; an attempt to prepare an ammonium hydroxide from ethylcarpaïne ethiodide was unsuccessful.

Nitrosocarpaïne, $\text{NO} \cdot \text{C}_{14}\text{H}_{24}\text{NO}_2$, crystallises from alcohol in colourless prisms melting at 144—145°. The compound is neutral, and exhibits Liebermann's reaction.

Carpaïne does not react with benzoic chloride or acetic chloride, but on treatment with acetic anhydride, a compound is formed which has not yet been investigated. Ammonia and an acid free from nitrogen are formed by the oxidation of carpaïne with sulphuric acid and potassium permanganate.

J. B. T.

New Reaction of Eserine, and a Green Colouring Matter derived from it. By S. J. FERREIRA DA SILVA (*Compt. rend.*, 117, 330—331).—When a minute fragment of eserine or one of its salts is dissolved in a few drops of fuming nitric acid, a yellow solution is obtained, and when this is evaporated on a water bath, it becomes dark yellow, and the residue, when completely dried, is pure green. This reaction is characteristic of eserine, and is very delicate (compare *Abstr.*, 1891, 134). The green substance, which the author calls *chloreserine*, dissolves in water, and also in strong alcohol, forming non-fluorescent, green solutions, from which the original compound can be recovered by evaporation. When dissolved in strong nitric acid, it yields a violet-red solution which afterwards changes to greenish-yellow. The solution in dilute nitric acid is blood-red by reflected light, and greenish-yellow by transmitted light. Ammonia has no effect on the colour of the *chloreserine*.

When dissolved in water, alcohol, or dilute sulphuric acid, *chloreserine* shows a well defined absorption band in the red between λ 670 and λ 688, a broader but more nebulous band in the blue and violet between λ 400 and λ 418, and a very feeble band in the orange.

C. H. B.

Albumoses and Peptones. By W. KÜHNE (*Zeit. Biol.*, 29, 308—324).—The article is mainly polemical, and contests Pekelharig's assertion that peptone is after all only a portion of the albumoses. This view is supported by a number of fresh experiments, in which the different behaviour of peptones and albumoses towards metaphosphoric and trichloroacetic acids is the main point.

W. D. H.

Proteids of Wheat. By T. B. OSBORNE and G. VOORHEES (*Amer. Chem. J.*, 15, 392—471).—This paper contains an historical review of the subject, and a detailed account of the compounds extracted from various grades of wheat flour by dilute alcohol, water, a 10 per cent.

sodium chloride solution, and dilute potash, together with the methods adopted for precipitation, isolation, and estimation. The following is an abstract of the summary which is appended.

Wheat contains the following proteids. (1.) A globulin belonging to the class of vegetable vitellins, soluble in saline solutions, precipitated by dilution and by saturation with magnesium sulphate or ammonium sulphate, but not with sodium chloride, not coagulated below 100° , and only partially at that temperature. This proteid amounts to 0.6—0.7 per cent. of the wheat, and when dried at 100° , has the following percentage composition:—C 51.03, H 6.85, N 18.39, S 0.69, O 23.04. (2.) An albumin, coagulating at 52° , in which condition it contains, per cent., C 53.02, H 6.84, N 16.80, S 1.28, O 22.06. It differs from animal albumin in that its solutions are precipitated by saturation with sodium chloride or magnesium sulphate; it is not precipitated by dialysis. From 0.3 to 0.4 per cent. of it is present in wheat. (3.) A proteose, precipitated (after removing the globulin by dialysis, and the albumin by coagulation) by saturation with sodium chloride. On concentrating its solutions by ebullition, a coagulum was gradually developed; this constituted about 0.3 per cent. of the wheat, and contained, per cent., C 51.86, H 6.82, N 17.32, S and O 24.00. The filtrate from this proteose contained a similar substance to the extent of 0.2—0.4 per cent. of the seed, but it was not obtained in a pure condition. (4.) Gliadin, soluble in dilute alcohol, and forming about 4.25 per cent. of the seed. It contains, per cent., C 52.72, H 6.86, N 17.66, S 1.14, O 21.62. This compound is the gliadin of Taddei, and the plant gelatin of Dumas and Cahours. In an impure state it has been described by others as gluten, fibrin, gliadin, mucedin, insoluble phytalbumose, and mucin. It dissolves in distilled water to an opalescent solution, from which it is precipitated by the addition of sodium chloride. It is insoluble in absolute alcohol, but very soluble in 70—80 per cent. alcohol; water or strong alcohol precipitates it from this solution. It dissolves in very dilute acids and alkalis, and is precipitated from these solutions unchanged by neutralisation. This proteid is one on which the formation of gluten largely depends. (5.) Glutenin, insoluble in water, saline solutions, and dilute alcohol. This constitutes the remainder of the proteids of wheat, and amounts to 4—4.5 per cent. of the seed. It is soluble in dilute acids and alkalis, and is precipitated from such solutions by neutralisation. For purification, it is dissolved in 0.2 per cent. potash, precipitated by neutralisation, extracted with alcohol and ether, again dissolved in potash, the solution filtered, and once more precipitated. When thus prepared and dried at 110° , it contains, per cent., C 52.34, H 6.83, N 17.49, S 1.08, O 22.26. The same proteid has been named by others zymone, plant fibrin, gluten-fibrin and gluten-casein. (6.) Wheat gluten is composed of gliadin and glutenin as essential constituents. The gliadin with water forms a sticky medium, which is not wholly soluble in the presence of salts; the flour is bound by this medium, and the dough and gluten are rendered tough and coherent by it. The glutenin imparts solidity to the gluten, forming a nucleus to which the gliadin adheres, and from which it is not washed away by water.

Gliadin and starch, mixed in the proportion of 1 : 10, form a dough, but no gluten, so that the gliadin is washed away with the starch. Flour free from gliadin gives no gluten. Soluble salts are also essential to the formation of gluten, as gliadin is readily soluble in distilled water; the mineral constituents of the seed are sufficient to supply the necessary salts. (7.) No fermentative action occurs in the formation of gluten, for its constituents are found in the flour having the same properties and composition as in the gluten, even under those conditions which would be supposed completely to remove antecedent proteids, or to prevent fermentative action. All the phenomena heretofore attributed to ferment action are explained by the properties of the proteids themselves as they exist in the seed and in the gluten.

A. G. B.

Solutions of Fibrin. By M. ARTHUS and A. HUBER (*Arch. physiol.*, 1893, 447—454).—It is stated that saline solutions of fresh fibrin, especially in 1 per cent. solution of sodium fluoride, exhibit properties similar to those obtained when fibrin is digested by gastric or pancreatic juice. Fibrin coagulated by heat, or by alcohol, is not soluble in solutions of neutral salts.

W. D. H.

Composition of Hæmatin and of Hæmatoporphyrin. By M. NENCKI (*Chem. Centr.*, 1893, ii, 95—96; from *Arch. sci. biol.*, 2, 121—131).—A reply to various criticisms of the author's previous work on the subject. Hoppe-Seyler's crystalline hæmatin contains acetic acid (compare *Ber.*, 18, 601), that of the author amyl alcohol; the difference is due merely to the method of preparation.

J. B. T.

Wheat Diastase. By I. V. EGOROFF (*J. Russ. Chem. Soc.*, 25, 80—83).—Diastase was prepared by moistening wheat at 8°, and allowing it to germinate in the dark at 16°, the air-dried malt being then ground up and treated for 24 hours with twice its weight of alcohol of 30°. From the alcoholic extract, the diastase was precipitated in three portions by means of absolute alcohol, each portion being washed and dried separately. Fractionation was then pursued by dissolving in water and precipitating with alcohol, until the starch and albumen had been almost entirely removed. From 3500 grams of wheat, only 4 grams of diastase were obtained. Analysis yielded the following results.

		Calculated for ashless material.
Hydrogen	6.78 per cent.	7.1 per cent.
Carbon.....	40.24 "	42.18 "
Nitrogen	4.7 "	4.93 "
Sulphur.....	0.7 "	0.74 "
Phosphorus	1.45 "	—
Ash.....	4.6 "	—

Wheat diastase thus prepared is a white powder, with a faint, yellowish tint, and dissolves in water with formation of a slightly

opalescent solution. With guaiacum and peroxide of hydrogen, it gives a dark-blue coloration. Neither 75° alcohol, nor half-saturated salt solution, will extract diastase from gluten. J. W.

Reychler's "Artificial Diastase." By I. V. EGOROFF (*J. Russ. Chem. Soc.*, 25, 83—86).—The author has made experiments which show that by dissolving gluten in 0.2 per cent. potassium dihydrogen phosphate, or in 0.1 per cent. acetic acid, no fresh diastase is formed, and that the greater power possessed by these over aqueous solutions of converting starch into maltose is probably due to the development of a bacterium capable of effecting this fermentation. J. W.

Diastase. By N. LUBAVIN (*J. Russ. Chem. Soc.*, 25, 86—90).—The author confirms the observations made in the foregoing paper. J. W.

A Ferment in *Penicillium glaucum* resembling Emulsin. By E. GÉRARD (*J. Pharm.*, [5], 28, 11—12).—The impure mixture of ferments isolated by the usual process from mature *Penicillium glaucum* inverts cane sugar and converts starch into sugars, and, in addition, completely hydrolyses the glucosides, amygdalin and salicin. From the latter property, the presence of a ferment resembling emulsin is inferred. W. T.

JOURNAL OF THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON
PHYSICAL, INORGANIC, MINERALOGICAL,
PHYSIOLOGICAL, AGRICULTURAL,
AND
ANALYTICAL CHEMISTRY.

Committee of Publication:

H. E. ARMSTRONG, Ph.D., F.R.S.
WYNDHAM R. DUNSTAN, M.A., F.R.S.
F. S. KIPPING, D.Sc.
R. MELDOLA, F.R.S.
H. F. MORLEY, M.A., D.Sc.
HUGO MÜLLER, Ph.D., F.R.S.

W. H. PERKIN, LL.D., F.R.S.
W. J. RUSSELL, Ph.D., F.R.S.
J. MILLAR THOMSON, F.R.S.E.
T. E. THORPE, Ph.D., F.R.S.
W. P. WYNNE, D.Sc.

Editor:

C. E. GROVES, F.R.S.

Sub-Editor:

A. J. GREENAWAY.

Abstractors:

C. F. BAKER, Ph.D., B.Sc.
D. BENDIX.
A. G. BLOXAM.
C. H. BOTHAMLEY.
B. H. BROUGH.
H. G. COLMAN, Ph.D.
H. CROMPTON.
L. DE KONINGH.
W. D. HALLIBURTON, M.D., B.Sc.,
F.R.S.
A. HARDEN, M.Sc., Ph.D.
F. S. KIPPING, Ph.D., D.Sc.
A. R. LING.
D. A. LOUIS.
N. H. J. MILLER, Ph.D.

G. T. MOODY, D.Sc.
J. M. H. MUNRO, D.Sc.
T. G. NICHOLSON.
W. J. POPE.
E. W. PREVOST, Ph.D.
E. C. ROSSITER.
R. ROUTLEDGE, B.Sc.
M. J. SALTER.
W. TATE.
J. TAYLOR, B.Sc.
L. T. THORNE, Ph.D.
J. B. TINGLE, Ph.D.
J. WADE, B.Sc. (JN. W.)
J. WALKER, D.Sc., Ph.D. (J. W.)

1893. Vol. LXIV. Part II.

LONDON:
GURNEY & JACKSON, 1, PATERNOSTER ROW.
1893.

LONDON :
HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY,
ST. MARTIN'S LANE.

CONTENTS.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:—

PART II.

General and Physical Chemistry.

	PAGE
EYKMAN (J. F.). Refractometric Observations	ii, 1
HARTLEY (W. N.). Physical Character of the Lines of the Spark Spectra of the Elements	ii, 2
ROBERTSON (G. H.). The Plante Lead Sulphuric Acid Lead Peroxide Cell from a Chemical Standpoint	ii, 3
ARMSTRONG (H. E.) and G. H. ROBERTSON. The Plante Lead Sulphuric Acid Lead Peroxide Cell from a Chemical Standpoint	ii, 4
SCHUSTER (A.) and A. W. CROSSLEY. Electrolysis of Silver Nitrate in a Vacuum	ii, 4
TRAUBE (J.). Electrolytic Dissociation and Ionisation	ii, 4
HUTCHINS (C. C.). Absorption of Radiant Heat by Alum	ii, 5
KURNAKOFF (N. S.). Specific Heat of Carbonic Anhydride	ii, 5
BERTHELOT and MATIGNON. Heat of Combustion of Chlorine Com- pounds	ii, 5
BERTHELOT and MATIGNON. Glyoxylic or Dihydroxyacetic Acid	ii, 6
BERTHELOT. Heat of Combustion of Glycollic Acid	ii, 6
VIGNON (L.). Thermochemistry of Carbon Compounds of Mixed Functions	ii, 6
ZAKREZEVSKI (J. V.). Specific Gravity of Ice	ii, 7
DE SAPORTA (A.). Relation between the Sp. Gr. of an Acid or Saline Solu- tion and the Molecular Weight of the Dissolved Substance.	ii, 7
TOEPLER (M.). Specific Volume of Sulphur	ii, 8
LINEBARGER (C. E.). Relations between the Surface Tensions of Liquids and their Chemical Constitution	ii, 8
ANTOINE (C.). Tensions of Vapours.	ii, 9
PUSCHL (C.). Elasticity of Gases	ii, 9
KISTYAKOVSKY (V.). Velocity of Etherification	ii, 9
JAUMANN (G.). Attempt to found a Chemical Theory on a Basis of Physical Comparison	ii, 10
LANDOLT (H.) and H. JAHN. Molecular Refractive Power of Organic Compounds for Infinite Wave Length	ii, 57
SNOW (B. W.). Infra-Red Emission Spectrum of the Alkalis	ii, 58
BANCROFT (W. D.). E.M.F. of Oxidation Cells	ii, 58
BROWN (J.). Electrolytic Conductivity and Dissociation	ii, 59
HINRICHS (G.). Specific Heat of the Atoms and their Mechanical Con- stitution	ii, 59
STOHMANN (F.). Heat of Combustion of Organic Compounds	ii, 59
DE FORCRAND. Constitution of Phosphoric acid and the Thermal Value of its three Acid Functions	ii, 60
DE COPPET (L.). Temperature and Maximum Density of Aqueous Solu- tions	ii, 60

	PAGE
DE COPPET (L.). Temperature of Maximum Density of Mixtures of Alcohol and Water	ii, 61
RÜCKER (A. W.). Density and Composition of Sulphuric acid Solutions	ii, 61
TREVOR (J. E.). Dissociation Measurements of Feebly Dissociated Acids	ii, 62
DUNCAN (C.) and F. HOPPE-SEYLER. Diffusion of Oxygen and Nitrogen in Water	ii, 62
YOUNG (S.). Van der Waals's Corresponding States	ii, 63
GORE (G.). Method of measuring Loss of Energy due to Chemical Union	ii, 63
SPITZER (W.). Use of certain Colouring Matters for the Determination of Affinities	ii, 64
LESAGE (P.). Rate of Evaporation of Solutions of Sodium and Potassium Chlorides	ii, 64
KALECSINSZKY (A. v.). Continuous Gas Evolution Apparatus	ii, 65
COLSON (A.). Rotatory Power of Salts of Diamines	ii, 105, 106
FRIEDEL (C.). Rotatory Power of Salts of Diamines	ii, 105
WYROUBOFF (G.). Rotatory Power of Solutions	ii, 106
MILLER (L.). Transformation of Chemical into Electrical Energy	ii, 107
GLAZEBROOK (R. T.) and S. SKINNER. Clark Cell as a Standard of E.M.F.	ii, 107
KURLOFF (V.). Production of Hydrogen Peroxide in the Electrolysis of Aqueous Sulphuric acid	ii, 108
BERTHELOT. Heat of Combustion of Camphors	ii, 108
TANATAR (S.). Heat of Hydration of Maleic Anhydride	ii, 108
TANATAR (S.). Thermochemical Data for some Organic Acids	ii, 108
WIEDEBURG (O.). Theory of Diffusion	ii, 109
FISCHER (E.) and E. SCHMIDMER. Rise of Salt Solutions in Bibulous Paper	ii, 109
PICKERING (S. U.). Cryoscopic Behaviour of Weak Solutions. Parts V, VI, and VII	ii, 110
ETARD (A.). Melting Points of Solvents as the Inferior Limits of Solubilities	ii, 111
GRIMALDI (G. P.). Cailletet and Colardeau's Method of determining Critical Points	ii, 111
GOUY. Effects of Gravity on Fluids at the Critical Point	ii, 112
SPERANSKY (A.). Velocity of Sugar Inversion in presence of Acetic and Lactic Acids	ii, 112
PICTET (R.). General Method of Chemical Synthesis	ii, 112
EWAN (T.). Absorption Spectra of Copper Salts in Aqueous Solution	ii, 149
BROWN (J.). Difference of Potential at the contact of mutually reacting Liquids	ii, 149
HERROUN (E. F.). Electromotive Forces of Gold and of Platinum Cells	ii, 149
HITTORF (W.). Electromotive Force of Galvanic Combinations	ii, 150
CANTOR (M.). Chemistry of Secondary Batteries	ii, 150
GORE (G.). Chemical Equilibrium in Mixed Electrolytes	ii, 150
KABLUKOFF (I.). Conductivity of Electrolytes in various Solvents	ii, 151
ZELINSKY (N.). Electrolytic Conductivity of Stereoisomeric Acids	ii, 151
AMAGAT (E. H.). Laws of the Expansion of Liquids compared with those relating to Gases and the form of the Isothermals for Liquids and Gases	ii, 152
PRUD'HOMME (M.). Relation between Heats of Formation, and Temperatures of Reaction	ii, 152
STOHMANN (F.) and H. LANGBEIN. Thermochemistry of Isomeric Allyl and Propenyl Derivatives	ii, 153
THIELE (E.). Estimation of the Vapour Density of Iodine in Different Atmospheres	ii, 154
KABLUKOFF (I.). Vapour Pressure of Aqueous Alcoholic Solutions of Salts	ii, 154
PICKERING (S. U.). Density of Sulphuric Acid Solutions	ii, 155
PICKERING (S. U.). Diffusion of Substances in Solution	ii, 155

	PAGE
FRITZ (H.). Relations of the Physical and Chemical Properties of the Chemical Elements and Compounds	ii, 155
ANGELI (A.) and G. BOERIS. Influence of Electrolytic Dissociation on the Decomposition of Ammonium Nitrite in Aqueous Solutions.	ii, 155
PETERSEN (J.). Cryoscopy, &c., of Ammoniometallic Compounds	ii, 156
FERRATINI (A.) and F. GARELLI. Behaviour of Indole and some of its Derivatives with respect to Raoult's Law	ii, 156
CLAUS (A.). Stereochemistry of Nitrogen	ii, 157
KABLUKOFF (I.). Avidity of Acids in Aqueo-alcoholic Solutions	ii, 157
WALDEN (P.). Affinity of Organic Acids.	ii, 157
MENSCHUTKIN (N.). Influence of the Constitution of the Alcohols on the Velocity of Etherification	ii, 158
KABLUKOFF (I.) and A. TSAKONI [ZACCONI]. Rate of Sugar Inversion in Aqueo-alcoholic Solutions	ii, 160
MONTEMARTINI (C.). Reaction between Nitrites and the Salts of Hydroxylamine	ii, 160
RETGERS (J. W.). Isomorphism	ii, 161
BORNEMANN (G.). Aluminium Apparatus in the Laboratory	ii, 162
KAHLER (M.). New Drying Oven.	ii, 162
JAFFÉ (B.). Laboratory Apparatus for Distillation with Superheated Steam.	ii, 163
FÉRY (C.). Study of Chemical Reactions in a Liquid Mass by means of the Index of Refraction	ii, 201
LIVING (G. D.) and J. DEWAR. Spectrum of Liquid Oxygen and Refractive Indices of Liquid Oxygen, Nitrous Oxide, and Ethylene	ii, 201
HENRY (C.). Phosphorescent Zinc Sulphide as a Photometric Standard.	ii, 202
BAGARD (H.). Thermoelectric Phenomena between two Electrolytes	ii, 202
MITSCHEHLICH (A.). The Ignition Point	ii, 202
WALDEN (P.). Diffusion Phenomena with Precipitate Membranes	ii, 203
LINEBARGER (C. E.). Influence of the Concentration of the Ions on the Intensity of the Colour of Solutions of Salts in Water	ii, 203
GUYE (P. A.). Determination of the Molecular Weight at the Critical Point	ii, 204
GUYE (P. A.). Molecular Dissymmetry	ii, 204
TIGERSTEDT (A.). Simplification of the Process of Fractional Distillation	ii, 204
BALY (E. C. C.). Separation and Striation of Rarefied Gases under the Influence of the Electric Discharge	ii, 253
ZECCHINI (F.). Atomic Refractions of the Elements with respect to Sodium Light	ii, 253
GLADSTONE (J. H.). Molecular Refraction and Dispersion	ii, 254
BRÜHL (J. W.). Spectrochemistry of Nitrogen	ii, 254
COLSON (A.). Influence of Temperature on the Rotatory Power of Liquids	ii, 255
FRIEDEL (C.). Stereochemistry	ii, 255
LE BEL (J. A.). Alteration of the Sign of Optical Rotation	ii, 255
EXNER (F.). Electrochemical Investigations	ii, 255
VÈZES (M.). Electrometric Study of Potassium Hydrogen Triplatohexanitrite	ii, 256
GORE (G.). Relation of Volta Electromotive Force to Pressure	ii, 256
WAKEMAN (A. J.). Behaviour of Electrolytes in Mixed Solvents	ii, 257
MITSCHEHLICH (A.). The Temperature of Explosion	ii, 257
FREYER (F.) and V. MEYER. Ignition Temperature of Explosive Gases.	ii, 257
MEYER (V.). Temperature of Explosion of Gaseous Mixtures	ii, 258
LUDEKING (C.) and J. E. STARR. Specific Heat of Liquid Ammonia	ii, 258
LOUGUININE (W.). Specific Heat of Erythritol and Mannitol.	ii, 258
LE CHATELIER (H.). Heat of Formation of Arragonite	ii, 259
PETERSEN (E.). Heat of Dissociation of some Acids	ii, 259
SCHNEIDER (E. A.). Behaviour of Colloids in Organic Solvents at the Critical Temperature of the Solvent	ii, 259

SCHREINEMAKERS (F. A. H.). Graphical Deductions from the Solution Isotherms of a Double Salt and its Components	ii, 260
ROLOFF (M.). Applications of Beckmann's Boiling Point Method Apparatus	ii, 260
KUENEN (J. P.). Measurements of Van der Waals' Surface for Mixtures of Carbonic Anhydride and Methylic Chloride	ii, 260
KRONBERG (H.). Determination of the Molecular Weight from the Rate of Evaporation	ii, 261
LOOMIS (E. H.). A more exact Cryoscopic Method.	ii, 261
THILO (J.). Freezing Points of Sulphuric acid of different Concentrations	ii, 262
JONES (H. C.). Freezing Point of very Dilute Solutions	ii, 263
MARCHIS (L.). Mixtures of Ether and Water.	ii, 264
WRIGHT (C. R. A.). Determination of the Specific Gravity of Liquids	ii, 264
FULTON (H. B.). Specific Gravity Apparatus	ii, 264
TRAUBE (J.). Molecular Volumes of Dissolved Alkali Salts and their Relation to the Atomic Volumes of the Elements	ii, 264
LINEBARGER (C. E.). Dissociation of Salts into their Ions by Water of Crystallisation	ii, 265
THUGUTT (S. J.). Deviations from the Gaseous Laws in Solutions	ii, 265
ABEGG (R.). Diffusion in Aqueous Salt Solutions	ii, 265
SACHSE (H.). Explanation of Affinity	ii, 266
KASTLE (J. H.). Decomposition of Silver Chloracetate	ii, 266
SCHMIDT (G. C.). Periodic Law	ii, 267
LEDUC (A.). New System of Atomic Weights, partly based on the Direct Determination of the Molecular Weights	ii, 267
MICHAEL (A.). New Apparatus	ii, 267
TREY (H.). Hydrogen Sulphide Apparatus	ii, 268
KAYSER (H.) and C. RUNGE. Spectra of Aluminium, Indium, and Thallium	ii, 313
KAYSER (H.) and C. RUNGE. Ultra-Red Spectra of the Alkalis	ii, 313
LAPRAIK (W.). Absorption Spectra of Chromium Compounds	ii, 313
MOISSAN (H.) and J. VIOLE. An Electrical Furnace	ii, 314
BARUS (C.) and E. A. SCHNEIDER. Behaviour of Solid Colloidal Silver towards the Electrical Current	ii, 314
POTILITZIN (A.). Determination of the Melting Point of Inorganic Substances	ii, 314
REYCHLER (A.). Nature of Solutions	ii, 315
TURIN (V.). Influence of Gravity on the Concentration of Solutions	ii, 315
SPERANSKY (A.). Electrical Conductivity and Freezing Point of Aqueous Solutions of Fluorine Compounds	ii, 315
DE SANDERVAL. Dissociation of Sodium Chloride in presence of Heated Surfaces of Porous Clay	ii, 316
MARCHLEWSKI (L.). Rate of Diffusion of Dextro- and Lævo-rotatory Tartaric acid	ii, 316
HINRICHS (G.). Determination of the Atomic Weight by the Method of Limit	ii, 316
HINRICHS (G.). General Method for the Calculation of the Atomic Weight from the Data of a Chemical Analysis	ii, 317
OLSZEWSKI (K.) and A. T. WITKOWSKI. Optical Properties of Liquid Oxygen	ii, 353
ZECCHINI (F.). Refraction Constants of Phosphorus in the Free State and in its Compounds with Elements or Monovalent Groups	ii, 353
ZECCHINI (F.). Refraction Constants of the Acids of Phosphorus and their Sodium Salts	ii, 354
ARGNAN (A.). Influence of Temperature on the Rotatory Power of Liquids	ii, 354
KRAKAU (A. A.). Meidinger's Cells.	ii, 355
DIITE (A.). Leclanché's Battery	ii, 355
BRANDENBURG (H.). Abnormal Electromotive Forces of Mercury	ii, 356
KONOVALOFF (D.). Electrical Conductivity of Mixtures	ii, 356

	PAGE
BERTHELOT (D.). Electrical Conductivities of Phosphoric acid and of Alkali Phosphates	ii, 357
MEYER (L.). A small Air Thermometer for Laboratory use	ii, 357
HAASE (E.). Melting Point Determinations	ii, 357
OSTWALD (W.). Thermochemistry of the Ions	ii, 357
TANATAR (S.). Thermochemistry of α -Dibromopropionic acid	ii, 358
MATIGNON (C.). Thermochemical Investigation of Ureïdes derived from Acids containing two Carbon Atoms	ii, 358
MATIGNON (C.). Thermochemical Investigation of Polybasic Ureïdes and of Uric acid	ii, 360
MATIGNON (C.). General Results of the Thermochemical Study of the Ureïdes	ii, 362
VAN RIJN VAN ALKEMADE (A. C.). Graphical Treatment of some Thermodynamical Problems on Conditions of Equilibrium in Salt Solutions with Solid Phases.	ii, 363
RETGEES (J. W.). Determination of the Specific Gravity of Salts Soluble in Water	ii, 363
LESCOEUR (H.). Dissociation of Saline Hydrates and Analogous Compounds	ii, 364
ARRHENIUS (S.). Determination of the Electrolytic Dissociation of Salts by means of Solubility Experiments	ii, 364
WIJS (J. J. A.). Electrolytic Dissociation of Water.	ii, 364
OSTWALD (W.). Electrolytic Dissociation of Water.	ii, 365
NOYES (A. A.). Electrolytic Dissociation of Acid Salts	ii, 365
PICKERING (S. U.). Freezing Points of Sodium Chloride Solutions	ii, 365
JONES (H. C.). Freezing Points of very Dilute Solutions.	ii, 366
SCHRÖDER (I.). Dependence of the Solubility of a Solid on its Melting Point	ii, 366
NERNST (W.). Participation of a Solvent in Chemical Reactions	ii, 367
MEERBURG (J. H.). Permeability of Precipitated Membranes	ii, 367
WILDERMANN (M.). Cyclical Equilibria	ii, 367
TECLU (N.). Laboratory Burner	ii, 368
BARTHEL (G.). Light Petroleum Burner	ii, 368
PUKAL (W.). Clay Filters	ii, 368
SCHLOESING (T., Jun.). Hygroscopic Properties of Textile Fabrics	ii, 368
TECLU (N.). Determination of the Intensity of Rays	ii, 401
TRAPESONZJANZ (C.). Molecular Refraction of Compounds containing Nitrogen (Aldoximes : Ketoximes)	ii, 401
LIVEING (G. D.) and J. DEWAR. Spectra of the Flames of some Metallic Compounds.	ii, 401
COCHIN (D.). Flame Spectra of some Metals	ii, 402
DITTE (A.). Leclanché Battery	ii, 402
DITTE (A.). A Cadmium and Ammonium Chloride Battery	ii, 403
BROWN (J.). Voltaic Cells with Fused Electrolytes.	ii, 403
ZAHN (G. H.). Changes at the Boundary between Solutions of different Concentration during the Passage of an Electric Current	ii, 404
ANDREWS (T.). Electrochemical Effects on Magnetising Iron	ii, 404
RICHARZ (F.). Law of Dulong and Petit	ii, 404
MOISSAN (H.) and H. GAUTIER. Specific Heat of Boron	ii, 404
LEMOINE (G.). Ferric Chloride and Ferric Oxalate Solutions	ii, 405
LEMOINE (G.). Decomposition of Oxalic Acid by Ferric Salts under the Influence of Heat	ii, 405
PAŘÍZEK (A. P.) and O. ŠULE. Applications of Raoult's Law at the Boiling Points of Solutions	ii, 406
LELLMANN (E.) and A. GÖRTZ. Coefficients of Affinity of Organic Bases.	ii, 407
LELLMANN (E.) and J. SCHLIEMANN. Coefficients of Affinity of Organic Acids	ii, 407
FLAVITZKY (F.). Theory of Chemical Types	ii, 408
MEYER (L.). Lectures on Inorganic Chemistry arranged in accordance with the Natural System of the Elements	ii, 408

	PAGE
BILTZ (H.). Explosives	ii, 409
STAATS (G.). Influence of Frictional Electricity on the Formation of Amalgams	ii, 441
ARRHENIUS (S.). Electrolysis of Alkali Salts	ii, 441
SCHÖNRÖCK (O.). Magnetic Rotation of Liquids and Salt Solutions	ii, 442
RECKLINGHAUSEN (M. v.). Mercurial Thermometer for Temperatures up to 550°	ii, 443
MAHLKE (A.). Mercurial Thermometers to register up to 550°	ii, 443
BARTOLI and STRACCIATI. Specific Heat of Water	ii, 443
BERTHELOT and MATIGNON. Heats of Combustion of Gaseous Hydrocarbons	ii, 444
LOUGUININE (W.) and I. KABLUKOFF. Heat developed by the Combination of Bromine with Non-saturated Compounds	ii, 444
EARP (Miss A. G.). Boiling Points and Melting Points of Sulphur Compounds	ii, 445
TSURUTA (K.). Heat of Vaporisation of Hydrogen Chloride	ii, 445
JAHN (H.). Heat of Vaporisation of Organic Compounds	ii, 445
ALTSCHUL (M.). Critical Constants of some Organic Compounds	ii, 446
LANDOLT (H.). Vapour Pressures of Fatty Acids	ii, 446
TAMMANN (G.). Internal Pressure in Solutions	ii, 447
MEYERHOFFER (W.). Cryohydric Quintuple Points	ii, 447
JONES (H. C.). The Freezing Points of Dilute Solutions of Sodium Chloride	ii, 447
BLÜMCKE (A.). Labile Conditions of Equilibrium in Salt Solutions	ii, 447
ROGOFF (M.). Volume Changes in Aqueous Solutions	ii, 447
BREDIG (G.). Electrolytic Dissociation of Water	ii, 448
SHIELDS (J.). Hydrolysis in Aqueous Salt Solutions	ii, 448
MEYERHOFFER (W.). The Number of Saturated Solutions of a Double Salt	ii, 449
LINEBARGER (C. E.). Existence of Double Salts in Solution	ii, 450
BUGARSZKY (S.). Conditions of Chemical Equilibrium	ii, 450
EBERSBACH (F. P.). Affinity Coefficients of Aromatic Amidosulphonic acids	ii, 450
PICTET (R.). General Method of Chemical Synthesis	ii, 451
VAN DER PLAATS (J. D.). The Atomic Weights of Stas	ii, 451
LANDOLT (H.). Conservation of Mass in Chemical Changes	ii, 452
WITT (O. N.). New Laboratory Apparatus	ii, 452
ERNST (O.). New Tap for Vacuum Desiccators	ii, 453
NASINI (R.). Refractive Powers for a Ray of Infinite Wave-length	ii, 505
PAGLIANI (S.). Specific Inductive Capacities and Refraction Constants	ii, 505
FREUDENBERG (H.). Electromotive Force in Electrolytic Analyses	ii, 506
MAGNANINI (G.). Influence of Boric acid on the Electrical Conductivity of Aqueous Solutions of Organic Acids	ii, 506
WEINER (A.) and A. MIOLATI. Constitution of Metalamine Salts	ii, 507
SALADIN. Electrical Furnace	ii, 507
MOISSAN (H.). Fusion and Volatilisation of Metals and Oxides in the Electric Arc	ii, 507
OSTWALD (W.). Discoverer of the Method of determining the Density of Solids by Suspension	ii, 508
POTTLITZIN (A. L.). Formation of Supersaturated Solutions	ii, 509
KURNAKOFF (N. S.). Influence of Hydration on Solubility	ii, 509
WILDERMANN (M.). Non-electrolytic Dissociation in Solutions	ii, 509
MAGNANINI (G.). The Colour of the Ions	ii, 510
OMELYANSKY (V.). Influence of Dilution on the Velocity of Chemical Reactions	ii, 510
GUGLIELMO (G.). Vapour Tensions of Solutions of Sulphur and Phosphorus in Carbon Bisulphide	ii, 511
BARONI (S.). Determination of Molecular Weights by Beckmann's Method	ii, 511
GARELLI (F.) and A. FERRATINI. Phenanthrene as a Solvent in Cryoscopic Determinations.	ii, 512

	PAGE
SCHREINEMAKERS (F. A. H.). Cryohydric Temperatures . . .	ii, 512
NACCARI (A.). Osmotic Pressure . . .	ii, 513
ALVISI (U.). Relation between the Periodic Classifications of L. Meyer and Mendeléeff . . .	ii, 513
ALVISI (U.). Specific Gravities of the Elements in the Periodic System . . .	ii, 513
MOLINARI (E.). Stereochemistry or Motochemistry? . . .	ii, 513
CAMICHAEL (C.). Absorption of Light by Liquid Bromine . . .	ii, 561
GUYE (P. A.). Product of Asymmetry . . .	ii, 561
GUYE (P. A.). Rotatory Power of a Substance belonging to an Homologous Series . . .	ii, 561
GUYE (P. A.) and L. CHAVANNE. Rotatory Power of Ethereal Salts of Valeric and Glyceric acids . . .	ii, 561
FREUNDLER. Influence of Organic Solvents on Rotatory Power . . .	ii, 562
CARHART (H. S.). A One-Volt Standard Cell . . .	ii, 562
DE HEMPTINNE (A.). Electrical Conductivity of Flames and Gases . . .	ii, 563
DE VISSER (L. E. O.). Experiments with the Manocryometer . . .	ii, 563
PHOOKAN (R. D.). Speed of Vaporisation of Compounds in different Atmospheres . . .	ii, 564
REYCHLER (A.). Diffusibility of certain Gases through a Caoutchouc Membrane . . .	ii, 564
LIEBERMANN (L.) and S. BUGARSKY. Diffusion in Aqueous Solutions of Mixed Salts . . .	ii, 565
NOYES (A. A.). Dissociation Ratio of Salts . . .	ii, 565
PICKERING (S. U.). Freezing Point of Solutions of Sodium Chloride . . .	ii, 565
LEA (M. C.). Nature of certain Solutions and a new means of investigating them . . .	ii, 566
BUGARSKY (S.). Conditions of Chemical Equilibrium . . .	ii, 566
DE VISSER (L. E. O.). Lecture Experiment with the Manocryometer . . .	ii, 566
HAGEMANN (C. T. L.). New Extraction Apparatus . . .	ii, 567

Inorganic Chemistry.

RAYLEIGH (LORD). The Relative Densities of Hydrogen and Oxygen . . .	ii, 10
WARREN (H. N.). Preparation of Silicon and Aluminium Chlorides . . .	ii, 11
LEA (M. C.). Dehydration of Silver Oxide . . .	ii, 11
POTILITZIN (A.). Decomposition of Strontium Bromate by Heat . . .	ii, 11
KORMILITZIN (A.). Action of Silver Oxide on Magnesium Nitrate . . .	ii, 12
RICHARDS (T. W.). Atomic Weight of Copper . . .	ii, 12
WRIGHT (C. R. A.). Ternary Alloys . . .	ii, 15
GOOCH (F. A.) and E. W. DANNER. Certain Points in the Interaction of Potassium Permanganate and Sulphuric Acid . . .	ii, 15
ANDREWS (T.). Passive State of Iron and Steel . . .	ii, 16
SCHMIDT (G. C.). Action of Nitric Acid on Potassium Dichromate . . .	ii, 16
MAUMENÉ (E.). Ammonium Chromates . . .	ii, 17
L'HÔTE (L.). Preparation of Vanadyl Trichloride: Extraction of Vanadium from its Ores . . .	ii, 17
WARREN (H. N.). Refining Gold, Silver, and Platinum . . .	ii, 17
BILTZ (H.). Vapour Density of Halogen Halides at Low Temperatures . . .	ii, 65
SALAZAR and NEWMANN. Oxidation of Solutions of Hydrogen Sulphide . . .	ii, 66
LUNGE (G.) and L. MARCHLEWSKI. Influence of Nitric Peroxide on the Specific Gravity of Nitric acid . . .	ii, 66
EMICH (F.). Behaviour of Nitric Oxide at High Temperatures . . .	ii, 66
PEARCE (R.). Crystalline Compound of Arsenious and Sulphuric Anhydrides . . .	ii, 66
PETERMANN (A.) and J. GRAFTIAU. Carbonic Anhydride in the Air . . .	ii, 67
WELLS (H. L.) and H. L. WHEELER. Rubidium and Potassium Trihalides . . .	ii, 67
WELLS (H. L.) and H. L. WHEELER. Penthalides of the Alkali Metals . . .	ii, 68

	PAGE
WELLS (H. L.) and H. L. WHEELER. Cæsium and Rubidium Aurichlorides and Aurobromides	ii, 68
WHEELER (H. L.). Cæsium and Rubidium Iodates	ii, 68
WELLS (H. L.). Cæsium Mercury Halides	ii, 68
WELLS (H. L.) and H. L. WHEELER. Double Halides of Silver and the Alkali Metals	ii, 69
LEA (M. C.). Disruption of Silver Halides by Mechanical Force	ii, 69
FOERSTER (O.). Formation and Properties of Tetracalcium Phosphate	ii, 70
LE CHATELIER (H.). Dissociation of Barium Peroxide	ii, 71
HENRY (C.). Phosphorescent Zinc Sulphide	ii, 72
HAMPE (W.). Simultaneous Precipitation of Copper and Antimony by the Electric Current	ii, 72
COLSON (A.). A Limited Reaction	ii, 72
GUNTZ. Probable Presence of Iron Carbonyl in Coal-gas	ii, 73
SCHNEIDER (E. A.). A case of Solid Solution	ii, 73
BAUBIGNY (H.) and E. PÉCHARD. Dissociation of Chrome Alum	ii, 73
KELLER (H. F.) and E. F. SMITH. Atomic weight of Palladium	ii, 73
LAURIE (A. P.). Compound of Gold and Tin	ii, 74
MONTEMARTINI (C.). Combustion of Hydrogen in Nitrous Oxide	ii, 113
LÉGER (E.). Hydrogen Bromide	ii, 114
KOLOTOFF (S. S.). Constitution of Hydroxylamine	ii, 114
HODGKINSON (W. R.) and J. YOUNG. Action of Sulphurous Anhydride on Oxy-salts	ii, 115
NICKEL (E.). Graphochemistry of Gunpowder	ii, 115
JOANNIS (A.). Molecular Weights of Sodammonium and Potassammonium	ii, 115
LEA (M. C.). Silver Hemisulphate	ii, 115
LE CHATELIER (H.). Fusion of Calcium Carbonate	ii, 117
JOANNIS (A.). Fusion of Calcium Carbonate	ii, 117
BERTRAND (G.). Zinc oxides of Alkaline Earths	ii, 118
HODGKINSON (W. R.) and C. C. TRENCH. Action of Ammonia on Sulphates	ii, 118
SCHREINEMAKERS (F. A. H.). Double Salt of Lead and Potassium Iodides	ii, 118
MEYERHOFFER (W.). A New Double Salt	ii, 119
NICKEL (E.). Graphochemistry of Lime Soda Glasses	ii, 119
ROOZBOOM (H. W. B.). Hydrates of Ferric Chloride	ii, 119
POULENC (G.). Anhydrous and Crystalline Iron Fluorides	ii, 122
PLACET (E.). Preparation of Metallic Chromium by Electrolysis	ii, 122
MARCHETTI (G.). Cryoscopic Behaviour of Aqueous Solutions of Chromium Chlorides	ii, 122
BLOMSTRAND (C. W.). Complex Acids containing Pentavalent Iodine	ii, 122
PICCINI (A.). Action of Hydrogen Peroxide on Certain Fluorides and Oxyfluorides	ii, 124
MAURO (F.). Fluoroxymolybdates. The Non-existence of Cuprous Fluoride	ii, 124
FRIEDHEIM (C.) and R. MEYER. Preparation of Tungstates free from Molybdenum	ii, 125
CORMIMBŒUF (H.). Crystallised Sodium Titanates	ii, 125
DITTE (A.) and R. METZNER. Action of Antimony on Hydrochloric acid	ii, 126
PETERSEN (E.). Double Halogen Compounds of Gold	ii, 126
CARLGREN (O.) and T. P. CLEVE. Some Platinum-Ammonium Compounds	ii, 127
CARRARA (G.). Molecular Weight and Refractive Power of Hydrogen Peroxide	ii, 163
HINRICHS (G.). Critical Examination of the Fundamental Determinations of Stas on Potassium Chlorate	ii, 163
OUVRARD (L.). Phosphorus Iodosulphide	ii, 164
HUGHES (R. E.). Properties of Dry Hydrogen Sulphide	ii, 164

LUCKOW (C.). Action of Potassium Permanganate on Sodium Thio- sulphate	ii, 164
CRAMER (E.). Volatilisation of Silica	ii, 164
LEDUC (A.). Density of Carbonic Oxide and the Atomic Weight of Carbon	ii, 165
HILGARD (E. W.). Formation of Alkali Carbonates in Nature	ii, 165
KOHLRAUSCH (F.). Solutions of Sodium Silicates	ii, 166
LE CHATELIER (H.). Fusion of Calcium Carbonate.	ii, 166
JOANNIS (A.). Fusion of Calcium Carbonate	ii, 167
MOISSAN (H.). Action of a High Temperature on Metallic Oxides	ii, 167
ROSENFELD (M.). Decomposition of Aqueous Vapour by Magnesium	ii, 168
STOCKLASA (J.). Monomagnesium Phosphate	ii, 168
LORIMER (W. S.) and E. F. SMITH. Determination of the Atomic Weight of Cadmium	ii, 168
SPRING (W.). Possibility of the Existence of certain Metals in the Gaseous Condition at Temperatures below their Fusing Points	ii, 168
MARCHLEWSKI (L.) and J. SACHS. New Formation of Basic Sulphates of Copper	ii, 169
BUCHERER (A. H.). Formation of Aluminium Sulphide	ii, 169
VAN BEMMELEN (J. M.) and E. A. KLOBBIE. Amorphous, Hydrated Ferric Oxide; Crystalline Ferric Hydroxide; Potassium and Sodium Ferrites	ii, 169
SMITH (E. F.). Action of Metallic Molybdenum and Tungsten on Solu- tions of Silver, Gold, and other Metals	ii, 170
POLECK (T.) and B. GRÜTZNER. A Crystalline Alloy of Iron and Tung- sten	ii, 170
CORMIMBŒUF (H.). Action of Potassium and Sodium Hydroxides on Antimony Trioxide	ii, 171
DITTE (A.) and R. METZNER. Action of Bismuth on Hydrochloric acid	ii, 172
JOLY (A.). Ammoniacal Derivatives of Ruthenium Chloride	ii, 172
MEINEKE (C.). Preparation of Pure Iodine	ii, 204
MOISSAN (H.). Physical Properties of Fluorine	ii, 204
SENDERENS (J. B.). Action of Sulphur in presence of Water on Salts of Polybasic Acids	ii, 205
PŔIWOZNIK (E.). Tellurium	ii, 205
MARCHLEWSKI (L.). Nitrous acid in Nitric acid	ii, 206
VITALI (D.). Action of Hydrogen Arsenide, Antimonide, and Phosphide on Silver Nitrate	ii, 206
RIMBACH (E.). Atomic Weight of Boron	ii, 207
LEA (M. C.). Silver	ii, 207
LEA (M. C.). Silver Chloride	ii, 208
HUGHES (R. E.) and F. R. L. WILSON. Action of Dried Hydrogen Chloride on Iceland Spar	ii, 208
MIJERS (J.). Constitution of Bleaching Powder as elucidated by its Dis- sociation	ii, 209
BARTHE and FALIÈRES. Complete Elimination of Barium from Strontium Salts	ii, 209
PASCHKOWEZY (S.). Magnesium Nitride	ii, 209
LESCŒUR (H.). Purification of Arsenical Zinc.	ii, 209
TERREIL (A.). Preparation of Acicular Basic Zinc Nitrate	ii, 209
SPRING (W.) and M. LUCON. Dehydration of Copper Hydroxide and certain of its Basic Salts in the presence of Water	ii, 210
NORDENSKIÖLD (A. E.). Molecular Weight of Gadolinium Oxide	ii, 211
HEADDEN (W. P.). Alloys of Iron and Tin	ii, 211
MARCHLEWSKI (L.) and J. SACHS. Roussin's Salt	ii, 211
REMMLER (H.). Cobalt	ii, 211
KRÜSS (G.) and F. W. SCHMIDT. Determination of the Atomic Weight of Nickel	ii, 212
PICCINI (A.). Action of Hydrogen Fluoride on certain Fluorides and Oxyfluorides	ii, 213

VÈZES (M.). An Acid Potassium Platonitrite	ii, 213
WILM (T.). Rhodium Salts	ii, 213
ANTONY (U.). Action of Chlorine and Carbonic Oxide on Iridium	ii, 214
TRAUBE (W.). Amide and Imide of Sulphuric acid	ii, 268
THRELFALL (R.). Preparation of Pure Nitrogen and Attempts to condense it	ii, 270
VAN DEVENTER (C. M.). Preparation of Nitric Oxide	ii, 271
LEDUC (A.). Density of Nitric Oxide	ii, 272
FREER (P. C.) and G. O. HIGLEY. Reduction of Nitric acid by Copper	ii, 272
STOKES (H. N.). Amidophosphoric acid	ii, 272
WATSON (G.). Preparation of Phosphoric acid	ii, 272
LEFÈVRE (C.). Crystalline Arsenates	ii, 273
MOISSAN (H.). Preparation of Carbon under High Pressure	ii, 275
FRIEDEL (C.). Reproduction of Diamonds	ii, 276
VAN DER HEIDE (J. K.). Potassium Astrachanite	ii, 276
ZAHORSKY (B.). Calcium Oxychloride	ii, 276
LUNGE (G.). Constitution of Bleaching Powder	ii, 277
STOKLASA (J.). Monomagnesium Phosphate	ii, 277
DENIGÈS (G.). Preparation of Sulphites of Zinc, Magnesium, and Cadmium	ii, 277
HINRICHS (G.). Stas's Determinations of the Atomic Weight of Lead	ii, 277
HERTY (C. H.). Mixed Double Haloids of Lead and Potassium	ii, 278
SEUBERT (K.) and M. ELTEN. Thallium Sulphite	ii, 278
NICKEL (E.). Graphochemical Calculation	ii, 278
BALESTRA (E.). Action of Potassium Iodide or Sodium Thiosulphate on Mercurammonium Salts	ii, 278
DITTE (A.). Decomposition of Alkali Aluminates in presence of Alumina	ii, 278
DITTE (A.). Decomposition of Alkali Aluminates by Carbonic acid	ii, 279
LACHAUD (M.) and C. LEPIERRE. Action of Hydrogen Ammonium Sulphate on Glass	ii, 280
ROUSSEAU (G.). Action of Water Vapour on Ferric Chloride.	ii, 280
SCHROEDER VAN DER KOLK (J. L. C.). Mixed Crystals of Ammonium and Ferric Chlorides	ii, 280
MOISSAN (H.). Preparation of Chromium and Manganese at a High Temperature	ii, 281
PREINZ (W.). Crystalline Forms of Chromium and Iridium	ii, 281
POULENC (C.). Chromium Fluorides	ii, 281
KEHRMANN (F.). Complex Inorganic Acids	ii, 282
FRIEDHEIM (C.). Molybdoarsenates	ii, 282
MOISSAN (H.). Preparation of Uranium at a High Temperature	ii, 283
KRÜSS (G.). Determinations of Equivalents by Conversion of Oxides into Sulphates. Separation of the Gadolinite Metals	ii, 283
KRÜSS (G.). Electrolysis of Solutions of the Rare Earths	ii, 284
KRÜSS (G.) and F. W. SMITH. Double Halogen Compounds of Gold	ii, 284
BORNTRÄGER (H.). Rapid Reduction of Potassium Platinochloride	ii, 284
JOLY (A.) and E. LEIDIÉ. Atomic Weight of Palladium	ii, 284
JOLY (A.). Physical Properties of Fused Ruthenium	ii, 285
THIELE (J.). Action of Ammonia on Hypochlorites	ii, 317
BEILL (A.). Influence of Temperature on the Formation of Ozone	ii, 317
MUTHMANN (W.) and J. SCHÄFER. Selenium Compounds	ii, 318
WISLICENUS (W.). Hydroxylamine	ii, 318
MOISSAN (H.). Properties of Diamonds	ii, 319
MOISSAN (H.). The Ash of Diamonds	ii, 319
LUZI (W.). Graphite and Graphitite	ii, 320
MOISSAN (H.). Intumescent Graphite	ii, 320
MUTHMANN (W.). Preparation of Pure Rubidium Salts	ii, 321
POULENC (C.). Zinc and Cadmium Fluorides	ii, 321
WELLS (H. L.). Cesium and Potassium Lead Haloids	ii, 322
LEPIERRE (C.). Atomic Weight of Thallium	ii, 322

	PAGE
JÄGER (W.). Purification of Mercury	ii, 322
DE BOISBAUDRAN (L.). Samarium	ii, 323
DITE (A.). Industrial Preparation of Alumina	ii, 324
MUTHMANN (W.). Preparation of Barium Permanganate	ii, 324
JOLY (A.) and M. VÉZES. Osmium	ii, 324
TALBOT (H. P.) and H. R. MOODY. Hydrogen Peroxide Solutions	ii, 369
CASPARI (R.). Preparation of Perchloric acid	ii, 369
BODENSTEIN (M.) and V. MEYER. Decomposition of Gaseous Hydrogen Iodide by Heat	ii, 369
CURTIUS (T.). Azoimide from Hydrazine Hydrate and Nitrous acid	ii, 372
CURTIUS (T.). New Synthesis of Azoimide	ii, 372
PAAL (C.). Hyponitrous acid	ii, 372
MIJERS (J.). Constitution of Bleaching Powder	ii, 372
LUNGE (G.). Formula of Bleaching Powder	ii, 372
WARREN (H. N.). Silicon	ii, 372
LUBAVIN (N.). Distribution of Calcium and Magnesium in Nature	ii, 373
HELMOLT (H. v.). Double Fluorides	ii, 373
KOSMANN (B.). Dehydration of Cupric Hydroxide and its Bibasic Salts	ii, 374
SABATIER (P.) and J. SENDERENS. Nitrocopper	ii, 374
RETGERS (J. W.). Solubility of Mercuric Iodide in Iodomethane	ii, 374
HOFMANN (K.) and G. KRÜSS. Action of Charcoal on Solutions of Salts of the Rare Earths	ii, 374
KRÜSS (G.) and A. LOOSE. Behaviour of the Gadolinite Earths with Potassium Chromate	ii, 375
KRÜSS (G.). Action of Aniline and Aniline Hydrochloride on the Gad- olinite Earths	ii, 376
KRÜSS (G.). Erbium	ii, 376
KLAUDY (J.). Behaviour of Aluminium towards Mercuric Salts	ii, 376
LORENZ (R.) and F. HEUSLER. Volatility of Manganese at High Temper- atures	ii, 377
LENORMAND (C.). Iron Chlorobromide	ii, 377
FRIEDHEIM (C.). History of the Complex Inorganic Acids	ii, 378
KEHRMANN (F.). Complex Inorganic Acids	ii, 378
HILLEBRAND (W. F.). Preparation and Specific Gravity of Uranium Dioxide	ii, 378
HILLEBRAND (W. F.). Further Example of the Isomorphism of Thorium and Uranium Dioxides	ii, 378
RETGERS (J. W.). Solubility of Metallic Iodides, &c., in Methylenic Iodide	ii, 378
HOFMANN (K. B.). Specific Gravity of Titanium	ii, 379
KRÜSS (G.). Formation of Thiovanadates	ii, 379
WERNER (A.). Constitution of Inorganic Compounds	ii, 379
ANTONY (U.). Composition of the Precipitate obtained with Hydrogen Sulphide in Solutions of Potassium Iridiochloride	ii, 379
ANTONY (U.). Lithium Iridiochloride and Iridium Bisulphide	ii, 380
MORAHT (H.) and C. WISCHIN. Osmium	ii, 380
LEDUC (A.). Densities and Molecular Volumes of Chlorine and Hydro- gen	ii, 410
WARREN (H. N.). Combinations of Oxygen and Hydrogen	ii, 410
DIETMAR (W.) and J. B. HENDERSON. Gravimetric Composition of Water	ii, 410
TRAUBE (M.). Production of Hydrogen Peroxide by Spontaneous Oxida- tion of Zinc: Combustion in Oxygen	ii, 412
TRAUBE (M.). Constitution of Hydrogen Peroxide and of Ozone	ii, 413
TRAUBE (M.). Sulphuryl Peroxide (Holoxide)	ii, 413
VELEY (V. H.). Conditions of the Formation and Decomposition of Nitrous Acid	ii, 413
LUZI (W.). Graphite	ii, 414
MUTHMANN (W.). Rubidium Salts	ii, 414
POULENC (C.). Fluorides of the Alkaline Earths	ii, 414
FRIEDRICH (H.). Lead Tetrachloride	ii, 415

	PAGE
WRIGHT (C. R. A.). Ternary Alloys	ii, 415
ROUSSEAU (G.). Basicity and Functions of Manganous Acid	ii, 416
LINEBARGER (C. E.). Hydrates of Manganous Sulphate	ii, 417
ORNDORFF (W. R.) and J. WHITE. Molecular Weight of Hydrogen Peroxide	ii, 453
GASSMANN (A.). Hydrogen Bromide	ii, 453
LEDUC (A.). Densities of certain Gases and the Composition of Water	ii, 453
BRUNCK (O.). Formation of Ozone at High Temperatures	ii, 454
GAL (J.). Plastic Sulphur from Sulphur Vapour	ii, 455
SEUBERT (K.) and M. ELTEN. Basic Metallic Sulphates	ii, 455
PÉLABON (H.). Absorption of Hydrogen Selenide by Liquid Selenium at High Temperatures	ii, 457
WHEELER (H. L.). Double Halogen Compounds of Tellurium with Potassium, Rubidium, and Cæsium	ii, 457
RETGERS (J. W.). Crystalline Nature of Red Phosphorus	ii, 457
MUTHMANN (W.). Red Phosphorus	ii, 458
RECKLINGHAUSEN (M. v.). Phosphorus Sulphides	ii, 458
GLATZEL (E.). Normal Thiophosphates	ii, 458
STAVENHAGEN (A.). Compounds of Arsenious and Sulphuric Anhydrides	ii, 459
WARREN (H. N.). Manufacture of Borax	ii, 460
REISCHLE (A.). New Alkali Borates	ii, 460
SCHUTZENBERGER (P.). The Volatilisation of Silica	ii, 460
ERNST (R.). Combustion of Carbon in Air	ii, 461
JOANNIS (A.). Action of Oxygen on Sodammonium and Potassammonium	ii, 462
HUGHES (R. E.). Water as a Catalyst	ii, 462
RICHARDS (T. W.). Atomic Weight of Barium	ii, 463
DUPONT (J.) and H. JANSEN. Copper Oxybromide analogous to Atacamite	ii, 463
HANNAY (J. B.). Metallurgy of Lead	ii, 464
NICKEL (E.). Graphochemical Calculation	ii, 464
CLASEN (A.) and B. ZAHORSKI. Action of Liquid Chlorine on Metallic Chlorides	ii, 464
HERTY (C. H.). Mixed Double Haloids of Lead and Potassium	ii, 465
KRÜSS (G.) and A. LOOSE. Approximate Determination of the Equivalents of Earths by Titration	ii, 465
PETTERSSON (O.). Anhydrous Chlorides of Metals of the Rare Earths	ii, 466
HOFMANN (K.) and G. KRÜSS. Terbia	ii, 466
HOFMANN (K.) and G. KRÜSS. Holmium Oxide	ii, 466
KLOBB (T.). Action of Heat on Zinc Permanganate	ii, 467
STORCH (L.). Reduction of Ferric Salts, and Solution of Ignited Ferric Oxide	ii, 468
ROUSSEAU (G.) and H. ALLAIRE. Iron Chloroborate, and Chloroborates Isomorphous with Boracite	ii, 468
DONATH (E.). Cobalt	ii, 468
WINKLER (C.). Elementary Nature of Nickel and Cobalt and their Atomic Weights	ii, 469
CHRISTENSEN (O. T.). Reactions with Ammonia at Low Temperatures	ii, 469
RECOURA (A.). Chromosulphuric, Chromotrisulphuric, and Chromosulphochromic acids	ii, 470
HAÜSSERMANN (C.). Sodium Perchromate	ii, 471
MOISSAN (H.). Preparation of Tungsten, Molybdenum, and Vanadium in the Electric Furnace	ii, 471
SMITH (E. F.) and V. OBERHOLTZER. Action of Hydrogen Haloids on Molybdic acid	ii, 471
FRIEDHEIM (C.). Phosphomolybdates	ii, 472
KEHRMANN (F.). Phospholutedtungstic acid	ii, 472
TROOST (L.). Preparation of Zirconium and Thorium	ii, 473
MITCHELL (C. A.). Black Antimony Trisulphide	ii, 473
PETERSEN (E.). Double Halogen Compounds of Gold	ii, 474

	PAGE
KRÜSS (G.) and F. W. SCHMIDT. Action of Chlorine and Bromine on Gold	ii, 474
WARREN (H. N.). Action of Silicon on Gold, Silver, Platinum, and Mercury	ii, 474
PETRENKO-KRITSCHENKO (P.). Palladium Sulphides	ii, 475
TANATAR (S.). Iodine Monochloride	ii, 514
RAYLEIGH (Lord). Densities of the Principal Gases	ii, 514
THOMSON (J. J.). Electrolysis of Steam	ii, 515
SCOTT (A.). Composition of Water by Volume	ii, 515
LEDUC (A.). Density of Sulphurous Anhydride	ii, 516
ELBS (K.). Preparation of Ammonium Persulphate	ii, 516
GHIRA (A.). Atomic Refraction of Boron	ii, 517
TARBLE. Combination of Boron Bromide with Phosphorus Tribromide	ii, 518
ROUSSEAU (G.) and H. ALLAIRE. Bromoborates	ii, 518
ROUSSEAU (G.). Cyclic Condensation of Carbon. Artificial Production of Diamond	ii, 519
HOLLEMAN (A. F.). Solubility of Insoluble Salts	ii, 519
GREENE (W. H.) and W. H. WAHL. Method for reducing Metallic Oxides	ii, 520
JOANNIS (A.). Action of Carbonic Oxide on Sodammonium and on Potassammonium	ii, 520
WELLS (H. L.). Quantitative Separation of Cæsium and the Preparation of Pure Cæsium and Rubidium Compounds	ii, 521
VILLIERS (A.) and F. BORG. Action of Zinc and Magnesium on Solutions of Metallic Salts. Estimation of Potassium	ii, 521
WRIGHT (C. R. A.). Ternary Alloys. Part VII	ii, 522
RANDALL (W. W.). Double Chlorides of Lead and Ammonium	ii, 523
WELLS (H. L.). Double Salts of Lead Tetrachloride	ii, 523
WELLS (H. L.) and W. R. JOHNSTON. Ammonium Lead Haloïds	ii, 523
WELLS (H. L.). Halogen Compounds of Potassium and Lead	ii, 524
WELLS (H. L.). Rubidium Lead Haloïds	ii, 524
LE CHATELIER (H.). Dissociation of Calcium Plumbate	ii, 524
WILDE (H.). Spectrum of Thallium	ii, 525
POULENC. Copper Fluorides	ii, 525
GRANGER (A.). Cuprous Phosphide	ii, 526
DEMARÇAY (E.). Simple Nature of Samarium	ii, 526
BOISBAUDRAN (L. DE). Samarium	ii, 526
ANTONY (U.) and P. DONNINI. Manganous Sulphide	ii, 527
GARNIER (J.). Influence of Electricity on the Carburization of Iron by Cementation	ii, 527
DE CLERMONT (P.). Oxidation of Nickel Sulphide	ii, 528
WYROUBOFF (G.). Potassium Tetrachromate and Ammonium Tetrachromate	ii, 528
RECOURA (A.). Chromopyrosulphuric acid	ii, 528
SMITH (E. F.) and V. LENHER. Action of Gaseous Ammonia on Molybdenyl Chloride	ii, 529
PÉCHARD (E.). Combination of Molybdates with Sulphurous acid	ii, 530
PÉCHARD (E.). Combination of Selenious acid with Molybdates. Molybdoselenious acid	ii, 530
SMITH (E. F.) and O. L. SHINN. Action of Gaseous Ammonia on Tungstyl Chloride	ii, 531
HEADDEN (W. P.). Tungstous Oxide, associated with Columbois Oxide	ii, 531
MOISSAN (H.). Volatilisation of Zirconia and Silica at a High Temperature, and their Reduction by Carbon	ii, 532
TROOST (L.). Extraction of Zirconium and Thorium Oxides	ii, 532
OUVRARD (L.). Arsenic Chlorosulphides and Antimony Chlorosulphides	ii, 533
OUVRARD (L.). Arsenic and Antimony Iodosulphides	ii, 533
MATHEY (E.). Metallurgy of Bismuth	ii, 534
WILM (T.). Gold Crystals containing Mercury	ii, 534
SZUHAY (J.). Iodide of Nitrogen	ii, 568

	PAGE
MARCHLEWSKI (L.). Existence of Nitrous acid in Aqueous Solution . . .	ii, 569
KOOIJ (D. M.). Decomposition of Gaseous Hydrogen Phosphide . . .	ii, 569
LÜBERT (H.). Hexametaphosphates	ii, 569
HELF (A.). Sulphides of Phosphorus	ii, 569
RETGERS (J. W.). Sublimation of Arsenic	ii, 570
MÜHLHAUSER (O.). Boron Carbide	ii, 570
MIXTER (W. G.). Behaviour of Charcoal with Halogens, Nitrogen, Sulphur, and Oxygen	ii, 571
SCHLAGDENHAUFFEN and BLOCH. Action of Aqua Regia on Carbon Bisulphide	ii, 571
BREDIG (G.). Molecular Weight of Potassium Persulphate	ii, 572
WHEELER (H. L.). Double Halogen Compounds of Arsenic with Cæsium and Rubidium; Compounds of Arsenic Trioxide with Cæsium, Rubi- dium, and Potassium Haloids	ii, 572
PIONCHON. Incomplete Oxidation of Aluminium	ii, 572
KLOBB (T.). Isomorphism amongst Anhydrous Alums	ii, 572
SCHNEIDER (E. A.). Ferric Phosphate	ii, 573
WINKLER (C.). Atomic Weights of Nickel and Cobalt	ii, 574
SMITH (E. F.) and H. L. DIECK. Crystalline Chromium Tungstate	ii, 574
SMITH (E. F.) and V. OBERHOLTZER. Action of Gases on Molybdenum and Tungsten	ii, 574
KEHRMANN (F.). Complex Inorganic Acids	ii, 574
KRÜSS (G.) and C. VOLK. Sulphur Compounds of Thorium	ii, 574
SCHNEIDER (E. A.). Variety of Gold Purple Soluble in Water	ii, 575

Mineralogical Chemistry.

LASPEYRES (H.). Beyrichite from Altenkirchen	ii, 18
LASPEYRES (H.). Cobaltiferous and Nickeliferous Iron Pyrites from Müsen	ii, 18
DOSS (B.). Pseudobrookite, Hämatite, and Anhydrite as Sublimation Products	ii, 18
LE NEVE FOSTER (E.). Soda from the Alkaline Waters of Owens Lake	ii, 18
MOROZIEWICZ (J.). Synthesis of Minerals of the Hauyn Group	ii, 19
TSCHERMAK (G.) and E. LUDWIG. The Chlorite Group	ii, 19
COHEN (E.) and E. WEINSCHENK. Meteoric Iron	ii, 20
MELVILLE (W. H.). Josephinite, a new Nickel-iron	ii, 75
PENFIELD (S. L.) and S. H. PEARCE. Polybasite and Tennantite from Aspen, Colorado	ii, 75
YEATES (W. S.) and E. F. AYRES. Plattnerite from Idaho	ii, 75
GENTH (F. A.). Penfieldite, a new Mineral Species	ii, 76
SMYTH (C. H., Jun.). The Clinton Iron Ore	ii, 76
PHIPSON (T. L.). Fluorine in Fossil Wood	ii, 76
WELLS (W. H.) and S. L. PENFIELD. Herderite from Hebron, Maine	ii, 76
REESE (C. L.). Formation of Phosphate Nodules	ii, 77
CROSS (W.) and L. G. EAKINS. New Occurrence of Ptilolite	ii, 77
CLARKE (F. W.). Constitution of Ptilolite and Mordenite	ii, 77
CLARKE (F. W.) and E. A. SCHNEIDER. Constitution of certain Micas and Chlorites	ii, 78
ORTON (E.). Quartz Boulder in Ohio Coal	ii, 78
BAYLEY (W. S.). Augite and Plagioclase in a Minnesota Gabbro	ii, 78
DILLER (J. S.). Mica-peridotite from Kentucky	ii, 79
MEUNIER (S.). Meteoric Iron from Hassi Iekna, Algeria	ii, 79
PRESTON (H. L.). New Meteorite from Kentucky	ii, 79
OWENS (W. G.). Meteorite from Central Pennsylvania	ii, 80
KUNZ (G. F.) and E. WEINSCHENK. Meteorite from Indian Valley Town- ship, Virginia	ii, 80

	PAGE
KUNZ (G. F.) and E. WEINSCHENK. Meteorite from the Sierra de la Ternerera, Chili	ii, 80
HILLEBRAND (W. F.). Zinc-bearing Spring Waters from Missouri	ii, 81
KYLE (J. J. J.). Vanadiferous Lignite in the Argentine Republic	ii, 128
CHROUSTCHOFF (K. V.). Artificial Production of Zircon	ii, 128
BODLÄNDER (G.). Cobaltiferous Chalybite from Neunkirchen	ii, 129
HEBERDEY (P. P.). Crystallised Slags from Raibl	ii, 129
MICHEL (L.). Artificial Production of Garnet (Melanite) and Sphene	ii, 129
IGELSTRÖM (L. J.). Friedelite from the Sjö Mine, Sweden	ii, 130
SCHMIDT (A.). Minerals of the Pyroxene Group	ii, 130
HAEFCKE (H.). Chemical Constitution of Hornblende	ii, 130
MICHEL (L.). Artificial Production of Rutile	ii, 173
KOSMANN (B.). Minerals from Lower Silesia	ii, 173
ZEMIATSCHEVSKY (P.). Palygorskite	ii, 174
BODLÄNDER (G.). Composition of Melilite	ii, 174
NORDENSKJÖLD (G.). Pholidolite from Sweden	ii, 174
FRIEDEL (C.). Existence of the Diamond in the Meteoric Iron of Cañon Diablo	ii, 174
AGRESTINI (A.). Hepatic Mineral Water and Mud of the Valle del Gallo	ii, 175
WARREN (H. N.). Artificial Production of Mineral Sulphides	ii, 214
GENTH (F. A.). Aguilarite	ii, 214
GENTH (F. A.). Metacinnabarite	ii, 215
GENTH (F. A.). Danalite	ii, 215
ROBINSON (F. C.). Phosphoric Acid in Beryl	ii, 215
HOWELL (E. J.). Mt. Joy Meteorite	ii, 216
MELIKOFF (P.) and C. SCHWALBE. Meteorite of Grossliebenthal	ii, 216
NATTERER (K.). Water and Sea-bottom Deposits of the Eastern Mediterranean	ii, 216
WERTH (J.). Origin of the Diamond	ii, 285
MOISSAN (H.). Graphite, Carbonado, and Microscopic Diamonds in Blue Earth from the Cape	ii, 285
SCHULZE (H.). Cupro-iodargyrite	ii, 285
DE BELL (J. T.). Cuproplumbite from Butte City, Montana	ii, 286
CLARKE (E. W.) and C. CATLETT. Platiniferous Nickel Ore from Canada	ii, 286
HUSSAK (E.). Brazilite	ii, 286
DE BELL (J. T.). Statuary Marble from Rutland, Vermont	ii, 286
JONES (A.). Electrical Calamine from Wythe Co., Virginia	ii, 286
GONNARD (F.). The Mesotype Group in the Puy-de-Dôme	ii, 287
BERKELEY (W. N.). Paranthrite from Clay Co., N. Carolina	ii, 287
CORSE (M. B.) and C. BASKERVILLE. Glauconite from Hanover Co., Virginia	ii, 287
CROSS (W.). Constitution of Spherulites in Acid Eruptive Rocks	ii, 287
MOISSAN (H.). The Meteorite from Cañon Diablo	ii, 288
FRIEDEL (C.). The Meteorite from Cañon Diablo	ii, 288
HEADDEN (W. P.). Stannite from the Black Hills, Dakota	ii, 325
HILL (R. T.). Hæmatite and Martite Iron Ores in Mexico	ii, 325
NAUFERT (A.) and W. WENSE. Minerals occurring in the Westeregeln Salt Beds	ii, 325
GENTH (F. A.). Anglesite associated with Boléite	ii, 326
NORDENSKJÖLD. Native Iron of Ovifak and the Bitumen in the Crystalline Rocks of Sweden	ii, 326
NICOLAS (C.). Sulphur Compounds in Mineral Waters of Barèges	ii, 326
KOLOTOFF (S.). Saline Constituents of Water from the Black Sea	ii, 326
BRÖGGER (W. C.). Sundite, a new Mineral from Oruro, Bolivia	ii, 382
IGELSTRÖM (L. J.). Melanostibian, a new Swedish Mineral	ii, 382
MALLARD (E.) and G. FRIEDEL. Melanophlogite	ii, 382
WEDEL (R.). Titaniferous Iron Ore from the Breitfirst	ii, 382
CUMENGE (E.). New Mineral from Boléo, Mexico	ii, 417

	PAGE
SCHRAUF (A.). Metacinnabarite from Idria	ii, 418
SCHERRER (F.). Arsenical Pyrites	ii, 418
SCHERBE (R.). Hauchecornite, a Nickel Bismuth Sulphide	ii, 418
GONNARD (F.). Zirconiferous Felspathic Inclusion in Basalt	ii, 418
BUISSAN (H. J.) and A. R. VAN LINGE. Phosphates from Florida	ii, 419
GAUTIER (A.). Phosphatic Rocks of Animal Origin and a New Type of Phosphorites	ii, 419
GAUTIER (A.). A New Type of Phosphorites	ii, 419
LINDSTRÖM (G.). Brandite and Friedelite	ii, 420
SJÖGREN (H.). Adelite and Svabite, New Swedish Minerals	ii, 420
SJÖGREN (H.). Långbanite	ii, 421
THUGUTT (S. J.). Mineral Chemical Studies	ii, 421
SJÖGREN (H.). Astochite	ii, 421
HAMBERG (A.). Astochite and Dahllite	ii, 421
LE CHATELIER (A.). Dioptase from the Congo	ii, 421
KENNGOTT (A.). Composition of Helvine	ii, 422
KENNGOTT (A.). Formula of Tourmaline	ii, 422
MOROZEWICZ (J.). Synthesis of Minerals	ii, 422
HUSSAK (E.). Zeolites from Brazil	ii, 422
MEUNIER (S.). Meteoric Iron from Augustinovka (Russia)	ii, 423
MOISSAN (H.). Iron from Ovifak	ii, 475
WILM (T.). Occurrence of Gold containing Palladium in the Caucasus	ii, 475
PENFIELD (S. L.). Three supposed new Sulphides of Iron and Nickel	ii, 535
PEMBERTON (H., Jun.) and G. P. TUCKER. Deposits of Native Soda near Laramie, Wyoming	ii, 535
MOSES (A. J.). Ettringite from Tombstone, Arizona	ii, 536
GAUTIER (A.). Formation of Natural Aluminium and Iron Phosphates	ii, 536
HEADDEN (W. P.). Kehoeite, a new Phosphate from South Dakota	ii, 537
PENFIELD (S. L.). Xenotime from El Paso Co., Colorado	ii, 537
HOBBS (W. H.). Rose-coloured Lime- and Alumina-bearing Tale	ii, 538
PENFIELD (S. L.). Zunyite from Colorado	ii, 538
PENFIELD (S. L.). Cookeite from Paris and Hebron, Maine	ii, 538
LINDGREEN (W.) and W. H. MELVILLE. Sodalite-syenite from Montana	ii, 538
KEMP (J. F.). Basic Dyke thought to contain Leucite	ii, 539
PIRSON (L. V.). Volcanic Rocks from Gough's Island, South Atlantic	ii, 539
LOCZKA (J.). Rock Salt from Deésakna	ii, 575
SCHARIZER (R.). Falkenhaynite, a new Mineral of the Wittichenite Group	ii, 576
STELZNER (A. W.). Franckeite, a new Ore from Bolivia	ii, 576
FRENZEL (A.). Kylindrite	ii, 576
WINKLER (C.). Artificial Minerals obtained in Chemical Industries	ii, 576
GAUTIER (A.). New Natural Phosphates	ii, 577
IGELSTRÖM (L. J.). Chondrostibian	ii, 577
BRUNLECHNER (A.). Descloizite from the Obir	ii, 577
MOSES (A. J.). Ettringite and Alabandine from Arizona	ii, 578
PISANI (F.). Idocrase	ii, 578
DILLER (J. S.). Peculiar Lava from Northern California	ii, 578
MEUNIER (S.). Two Turkish Meteorites	ii, 578
MELIKOFF (P.). Analysis of the Wawilowka Meteorite	ii, 579
GLÄSER (M.) and W. KALMAN. New Iodine Spring in Austrian Silesia	ii, 579

Physiological Chemistry.

MARCEY (W.). Absorption of Oxygen and Formation of Carbonic Anhydride in Human Respiration	ii, 20
LOEWY (A.). Action of Fatiguing Muscular Work on the Respiratory Interchange	ii, 21
MALLÈVRE (A.). Influence of Acetic Acid on Gaseous Metabolism	ii, 21
ZUNTZ (N.). Nutritive Value of Cellulose	ii, 22

	PAGE
LILIENFELD (L.). Researches on Blood	ii, 22
GEELMUYDEN (H. C.). Some Results of Transfusion	ii, 22
HARRIS (V. D.) and W. J. GOW. Pancreatic Juice in different Animals	ii, 22
SHORE (L. E.) and M. C. TEBB. Conversion of Maltose into Dextrose	ii, 23
BRANDL (J.) and H. TAPPEINER. Fluorine Compounds in the Organism	ii, 23
KUNKEL (A. J.). Absorption of Iron	ii, 23
MACALLUM (A. B.). Demonstration of the Presence of Iron in Chromatin by Microchemical Means	ii, 24
FRANK (O.). Absorption of Fats	ii, 24
STRASSMANN (F.). Nutritive Value of Alcohol	ii, 24
ZUNTZ (N.) and A. MAGNUS-LEVY. Digestibility and Nutritive Value of Bread	ii, 24
SEEGEN (J.). Formation of Sugar in the Liver	ii, 25
PFEIFFER (T.) and G. KALB. Deposition of Albumin during the Fattening of Full Grown Animals	ii, 25
LIEBERMANN (L.). Chemistry of the Kidney Substance	ii, 27
POLITS (G.). Asparagine as a Nutritive Substance	ii, 27
MAUTHNER (J.). Physiological Action of Asparagine	ii, 27
MAYER (A.). Influence of Sugar on the Constitution of Milk Fat	ii, 27
MAYER (A.). Melting Point and Composition of Butter from Cows variously fed	ii, 28
MAGGIORA (A.). Composition of Over-ripe Cheese	ii, 29
LIEBERMANN (L.). The Phosphates of Horse's Urine	ii, 30
HARLEY (V.). Obstructive Jaundice	ii, 30
GÉRARD (E.). Transformation of the Albumin of the Urine in Bright's Disease	ii, 30
CREMER (M.) and A. RITTER. Phloridzin Diabetes	ii, 31
HABLEY (V.). Pancreatic Diabetes	ii, 31
DUNCAN (C.) and F. HOPPE-SEYLER. Respiration in Fishes	ii, 81
PICKARDT (M.). Dextrose in Blood	ii, 81
GABRIEL (S.). Fluorine in Bones and Teeth	ii, 81
SALKOWSKI (E.). Relation of the Urinary Carbohydrates to Humous Substances	ii, 82
EMBDEN (H.). Alcaptonuria	ii, 82
USCHINSKY. Poisoning by Hydrogen Sulphide	ii, 83
EWALD (A.). Influence of Heat on Gas Exchange	ii, 131
GRANDIS (V.). Gaseous Tension in the Blood and Serum of Peptonised Animals	ii, 131
DE SAINT-MARTIN (L.). Elimination of Carbonic Oxide	ii, 131
WEISKE (H.). Influence of Increased or Diminished Consumption of Food, and of the Salts added to the Food, on Digestion and Resorption	ii, 132
HALLIBURTON (W. D.). Proteids of Kidney and Liver Cells	ii, 133
YOUNG (R. A.). Mucin in Bone	ii, 134
HEWLETT (R. T.). Lacto-globulin	ii, 134
LILIENFELD (L.) and A. MONTI. Microchemical Localisation of Phosphorus in the Tissues	ii, 135
IRISAWA (T.). Lactic acid in Blood and Urine	ii, 136
ARAKI (T.). Action of Phosphorus and Arsenious Oxide on the Animal Organism	ii, 136
SCHMITZ (C.). Putrefaction in the Intestine	ii, 137
GRIFFITHS (A. B.). Ptomaines from the Urine in Erysipelas and Puerperal Fever	ii, 137
HAMBURGER (H. J.). Influence of Acids and Alkalis on the Determination of the Osmotic Pressure in relation to the Red Blood Corpuscles	ii, 175
HUPPERT. Occurrence of Glycogen in Blood	ii, 176
MEYERHOLD (F. A.). Acid Reaction of Muscle	ii, 176

	PAGE
FÉRÉ (C.) and L. HERBERT. Accumulation of Potassium Bromide in the Organism	ii, 176
GABRIEL (S.). Nutritive Value of Asparagine	ii, 177
VOIT (K.). Nutritive Value of Asparagine	ii, 177
VOIT (F.). Metabolism in Diabetes Mellitus	ii, 177
VOIT (F.). Behaviour of Galactose in Diabetics	ii, 177
ROSENHEIM (T.). Occurrence of Ammonia in the Stomach Contents	ii, 177
ZOJA (L.). Uroerythrin and Hæmatoporphyrin in Urine.	ii, 178
CURCI (A.). Behaviour of Xylenes in the Organism	ii, 178
NENCKI (M.) and H. BOUTMY. Influence of the Carboxyl Group on the Toxic Action of Aromatic Compounds	ii, 178
GRÉHANT (N.) and E. MARTIN. Physiological Action of Opium Smoke	ii, 179
RICHTER (C.). Toxicity of certain Mineral Salts	ii, 179
BERTELS (A.). Influence of Chloroform on Peptic Digestion	ii, 217
ELLENBERGER and HOFMEISTER. Behaviour of Sterilised Milk towards Digestive Fluids.	ii, 217
FÉRÉ (C.) and L. HERBERT. Accumulation of Strontium Bromide in the Organism	ii, 217
FÉRÉ (C.) and L. HERBERT. Accumulation of Potassium Bromide in the Organism	ii, 217
ULLMANN. Localisation of Mercury in the Animal Organism.	ii, 217
ERNST (P.). Keratohyalin	ii, 218
ERNST (P.). Hyalin and Colloid	ii, 218
COHNSTEIN (W.). Alkalinity of the Blood during Muscular Work	ii, 218
DEWEVRE. Glycogenic Function in Winter Frogs	ii, 218
GEIGEL (R.) and L. ABEND. Secretion of Hydrochloric Acid in Nervous Dyspepsia	ii, 219
STARLING (E. H.). Lymph Secretion	ii, 219
KLINGEMANN (F.). Transmission of Alcohol to Milk	ii, 219
COLLIER (P.). Milk of Different Breeds of Cows	ii, 220
LASSAR-COHN. The Acids of Ox Gall	ii, 220
GAUBE (J.). Carbonated Albuminuria	ii, 221
GROVES (E. W.). Chemical Stimulation of Nerves	ii, 221
HOWELL (W. H.), Miss E. COOKE, and R. G. EATON. Action of Inorganic Salts on the Heart	ii, 221
LAPICQUE (L.). Physiological Action of Iodine Compounds	ii, 222
LAPICQUE (L.) and A. MALBEC. Action of Strontium Iodide on the Circulation	ii, 222
LAPICQUE (L.). Physiological Action of Iodides	ii, 222
HANRIOT and C. RICHTER. Physiological Action of Chloralose	ii, 222
MORAT (J. P.) and M. DOYON. Physiological Action of Atropine and Pilocarpine	ii, 222
ARNAUD and CHARRIN. Physiological Action of Cinchonamine Sulphate	ii, 223
GRIMAUX (E.) and J. V. LABORDE. Physiological Action of Cupreïne and its Derivatives	ii, 223
HALDANE (J.) and J. L. SMITH. Toxic Action of Expired Air	ii, 223
NILES (E. P.). Antiseptic Treatment of Wounds	ii, 223
DE SAINT MARTIN (L.). Elimination of Carbonic Oxide	ii, 288
SMITH (W. J.). Influence of certain Sulphur Compounds on Metabolism	ii, 288
MAXWELL (W.). Phosphorus and the Lecithins	ii, 289
BOUILLOT (J.). Alkaloids in Cod-liver Oil	ii, 290
BAUMANN (E.). Excretion of Ethereal Hydrogen Sulphates	ii, 290
NOËL PATON (D.). Crystalline Globulin occurring in Human Urine	ii, 290
PFLÜGER (E.). Origin of Fat from Proteid in the Body	ii, 327
PFLÜGER (E.). Nutrition with Carbohydrate and Flesh and with Carbohydrate alone	ii, 327
BREISACHER (L.). Amount of Albumin required for the Human Body	ii, 328
NORDEN (C. v.). Alcohol as a Substitute for Albumin under various conditions of Feeding	ii, 328
KLEIN. Feeding Experiments with Sunflower Cake on Cows	ii, 328

HEERLEIN (W.). Influence of Caffeine and Coffee Distillate on Metabolism	ii, 329
KRAKOW (N. P.). Influence of Ligature of the Bile Duct on Metabolism	ii, 329
HILDEBRANDT (H.). Hydrolytic Ferments	ii, 329
SALKOWSKI (E.). Synovia and Mucin	ii, 330
BLEIBTREU (M.) and L. BLEIBTREU. Method of estimating the Volume of the Corpuscles of the Blood	ii, 331
LANGE (O.). Volume of Blood Corpuscles	ii, 332
WENDELSTADT (H.) and L. BLEIBTREU. The Volume and Amount of Protein in single Red Blood Corpuscles	ii, 332
HAMBURGER (H. J.). Influence of Acids and Alkalis on Defibrinated Blood	ii, 332
BIAL (M.). Diastatic Action of the Serum of Blood and Lymph	ii, 333
RÖHMANN (F.). Diastatic Ferment in Lymph	ii, 333
FRÄNKEL (S.). Glycogen	ii, 333
SALOMON (G.). Occurrence of Glycogen in Blood	ii, 333
ABEL (J. J.) and A. MUIRHEAD. Carbamic acid in the Urine after Ingestion of Calcium Hydroxide	ii, 333
BERNHEIM (A.). Exudations and Transudations	ii, 334
GASCARD (A.). Calculus in Muscle	ii, 334
DANILEWSKY (B.). Physiological Action of Cocaine	ii, 334
GUINARD (L.). Resistance of Goats to the Action of Morphine	ii, 335
FRÄNKEL (E.) and F. REICHE. Sulphuric acid poisoning	ii, 335
ADRIAN (C.). Influence of dividing the Daily Nutriment on the Metabolism of the Dog	ii, 383
PANORMOFF (A.). Sugar in Muscle	ii, 383
SCHAEFFER. Goat's Milk	ii, 383
LASSAR-COHN. The Acids of Ox Bile	ii, 383
WULFF (C.). Uric acid in the Organism	ii, 384
CASH (J. T.) and W. R. DUNSTAN. Action of Nitrites on Muscle	ii, 384
CHITTENDEN (R. H.) and G. L. AMERMAN. Artificial and Natural Digestion	ii, 423
PICKERING (J. W.). Physiology of the Embryonic Heart	ii, 424
MÖRNER (C. T.). Proteids of the Crystalline Lens	ii, 424
GOURLAY (F.). Proteids of the Spleen and Thyroid	ii, 425
HAMBURGER (H. J.). Action of Physiological Saline Solution on Blood Corpuscles	ii, 426
WRIGHT (A. E.). Coagulation of Blood	ii, 426
STOCKMANN (R.). Iron in Chlorosis	ii, 427
MÖRNER (C. T.). Action of Drugs containing Iron	ii, 427
EBSTEIN (W.). Physiological Action of Pentoses	ii, 427
COOKE (W. W.) and J. L. HILLS. Abnormal Milk	ii, 428
HELME (T. A.). Fœtal Urine	ii, 428
ARAKI (T.). β -Hydroxybutyric Acid in the Organism	ii, 428
SALOMON (G.). Formation of Uric acid	ii, 428
GRIMM (F.). Urobilin	ii, 429
REID (E. W.). Mucin Granules of <i>Myxine glutinosa</i>	ii, 429
SCHIERBECK (N. P.). Influence of Carbonic Anhydride on the Diastatic and Peptone-forming Ferments in the Animal Organism	ii, 475
CAMERER (W.). Metabolism in a Child 14 months old	ii, 476
PRAUSNITZ (W.). Metabolism during Inanition	ii, 477
LEHMANN (C.), F. MUELLER, I. MUNK, H. SENATOR, and N. ZUNTZ. Physiology of Starvation	ii, 477
HALLIBURTON (W. D.). Proteids of Nervous Tissue	ii, 478
LOCKE (F. S.). Action of Sodium Oxalate on Voluntary Muscle	ii, 480
PRAUSNITZ (W.). Phloridzin Diabetes	ii, 480
CREMER (M.). Phloridzin Diabetes in Frogs	ii, 480
CREMER (M.) and A. RITTER. Phloridzin Diabetes	ii, 480
GARROD (A. E.). Urinary Hæmatoporphyrin	ii, 480

	PAGE
HILDEBRANDT (H.). Nutritive Value of Albumoses.	ii, 539
KRAUSS (E.). Nutritive Value of Proteïds	ii, 540
HIRSCHFELD (F.). Proteïd in Diet	ii, 540
SCHULTZ-SCHULTZENSTEIN (C.). Influence of Tea and Coffee on Artificial Digestion	ii, 540
MARTIUS (F.). Occurrence of Hydrochloric acid in the Stomach	ii, 540
OLIVER (T.) and F. C. GARRETT. Gases of Blood during Anæsthesia	ii, 540
JONES (E. L.). Chlorosis	ii, 541
HALLIBURTON (W. D.) and T. G. BRODIE. Intravascular Coagulation	ii, 541
FAYRER (J.). Cardiac and Pulmonary Thrombosis	ii, 541
HUPPERT. Glycogen in Blood and Pus	ii, 541
NOËL PATON (D.). Influence of Fever on Hepatic Glycogen	ii, 541
THOMPSON (W. H.). The Work of the Kidney	ii, 542
BAIRSCH (K.). The Carbohydrates of Normal Urine	ii, 542
SALOMON (G.). Episarkine	ii, 542
HARLEY (V.). Diabetic Coma	ii, 543
WRAMPELMEYER (E.). Amount of Lecithin in Butter	ii, 543
HARNACK (E.) and J. REMERTZ. Influence of Chloral Hydrate and Amylene Hydrate on Metabolism	ii, 543
COHN (R.). Physiological Action of Pyridine and Naphthalene Derivatives	ii, 544
COHN (R.). A Complete Process of Reduction occurring in the Animal Tissues	ii, 544
MARCEY (W.). Exercise and Respiratory Interchange	ii, 579
GABRIEL (S.). Influence of Sodium Chloride on the Digestibility and Assimilation of Proteïd	ii, 579
WOLFF (E. V.) and J. EISENLOHR. Effect of Salt on Digestion	ii, 580
MAGNUS-LEVY (A.). Digestibility of Milk and Proteïd	ii, 580
GRAFFENBERGER (L.). Influence of Light on Metabolic Processes	ii, 580
GARROD (A.). Urea in the Blood of Birds	ii, 581
BIAL (M.). Diastatic Ferment in Blood	ii, 581
SAAKE (W.). Glycogen	ii, 581
BRANDL (J.). Absorption from the Stomach	ii, 581
VOIT (F.). Secretion and Absorption in the Small Intestine	ii, 582
DUCLAUX. The Phosphates of Milk.	ii, 582
KLUG (F.) and V. OLASAVSKY. Effect of Work on the Excretion of Phosphoric acid	ii, 583
VITALI (D.). Transformations of Arsenious Anhydride in the Organism.	ii, 583
VITALI (D.). Absorption and Physiological Action of Arsenic Trisulphide	ii, 583
SMITH (W. J.). Physiological Action of the two Isomeric Ethylic Thiocarbamates	ii, 584
POMFRET (H. W.). Physiological Action of Organic Oximides	ii, 584
HARLEY (V.). Physiological Action of Sugar	ii, 584
CREMER (M.). Physiological Action of Sugars	ii, 585
HAIG (A.). Physiological Action of Uric acid	ii, 585
STOCKMAN (R.). Physiological Action of Quinoline and Isoquinoline	ii, 585
SMITH (F.). Dandruff of the Horse	ii, 585

Chemistry of Vegetable Physiology and Agriculture.

ARTHUR (M.) and A. HUBER. Difference between Formed and Unformed Ferments	ii, 31
BIERNACKI (E.). Influence of Antiseptics on Fermentation	ii, 32
NOBBE (F.), E. SCHMIDT, L. HILTNER, and E. HOTTER. The Power of Propagation of the Leguminous Bacteria in Soils	ii, 32
BOKORNY (T.). Assimilation of Formaldehyde by Green Plant Cells	ii, 32
HESSE (O.). Carotene	ii, 33
NOBBE (F.), E. SCHMIDT, L. HILTNER, and E. HOTTER. Physiological Meaning of the Root Nodules of <i>Eleagnus angustifolius</i>	ii, 33

	PAGE
PETERMANN (A.). The Nitrogen Question	ii, 33
KULISCH (P.). Chemical Composition of Apples and Pears, especially with regard to their Utilisation for Fruit Wine	ii, 37
DAVIDSON (R. J.). Chemistry of the Tobacco Plant	ii, 38
HASELHOFF. Manufacture and Composition of Linseed Cake and Meal	ii, 38
VAN PESCH (F. J.). Manufacture and Impurities of Linseed Cake	ii, 39
GRIFFITHS (A. B.). New Bacillus in Rain-water	ii, 83
BERTHELOT. Absorption of Atmospheric Nitrogen by Microbes	ii, 83
SCHLOESING (T., Jun.) and E. LAURENT. Absorption of Atmospheric Nitrogen by Plants	ii, 84
EWELL (E. E.). Carbohydrates of the Coffee Berry.	ii, 84
SIGMUND (W.). Relations between Fat-decomposing and Glucoside- decomposing Ferments	ii, 85
LIPPMANN (E. O. v.). An Acid in Beet Leaves	ii, 85
SCHULZE (E.). Nitrogenous Constituents of the Seedlings of <i>Vicia</i> <i>sativa</i>	ii, 85
SCHLOESING (T., Jun.). Interchange of Carbonic Anhydride and Oxygen between plants and the Atmosphere	ii, 137
SCHLOESING (T., Jun.) and E. LAURENT. Absorption of Free Nitrogen by Plants	ii, 138
DUCLAUX. Absorption of Free Nitrogen by Plants	ii, 138
BERTHELOT. Absorption of Free Nitrogen by Plants	ii, 138
BERTRAND (G.) and G. POIRAULT. Colouring Matter of Pollen	ii, 139
SCHULZE (E.). Carbohydrates in Leguminous Seeds	ii, 139
PALLADIN (W.). Ash in Etiolated Leaves	ii, 140
COLBY (G. E.) and H. P. DYER. Analysis of California Prunes, Apricots, and Peaches	ii, 140
WOLL (F. W.). Relative Value of Maize Silage and Field and Fodder Maize for Milk and Butter Production	ii, 141
WOLL (F. W.). Losses in ensiling and field-curing Maize	ii, 141
SCHLOESING (T.). Influence of the Distribution of Manures by the Soil on their Utilisation	ii, 141
BOIRET (H.) and G. PATUREL. Employment of Ferrous Sulphate in Agriculture.	ii, 142
GARROS (F.). Organised Ferment from Cherry Tree Gum. Pectinose	ii, 180
SCHLOESING (T., Jun.). Exchange of Carbonic Anhydride and Oxygen between Plants and the Atmosphere	ii, 180
MOORE (S. L. M.). Supposed Presence of Albumin in the Walls of Vege- table Cells	ii, 180
VAN WISSELINGH (C.). Cork and Suberin	ii, 181
POLECK (T.). Ethyl Alcohol in Oil of Roses	ii, 181
SHIMOYAMA (Y.) and H. ONO. Occurrence of Thymol in the Ethereal Oil of <i>Mosula Japonica</i>	ii, 181
MUNTZ (A.) and A. C. GIRARD. Loss of Nitrogen in Manures	ii, 181
HÉBERT (A.). Fermentation of Manure	ii, 182
GILLESPIE (A. L.). Bacteria of the Stomach	ii, 223
GIBSON (H. B.). Liberation of Nitrogen during Putrefaction	ii, 224
DE CHALMOT (G.). Soluble Pentoses in Plants	ii, 224
MAYER (A.). Production of Albumin in Plants	ii, 224
STROHMER (F.) and A. STIFT. Composition and Nutritive Value of the Tubers of <i>Stachys tuberosa</i>	ii, 225
PASSERINI (N.). Composition of the Stems and Leaves of Tomatoes. Presence of Boron, Lithium, and Copper in the Plant	ii, 225
PASSERINI (N.). Composition of Chick-Peas (<i>Cicer arietinum</i>). Pre- sence of Boron, Lithium, and Copper in the Plant	ii, 226
PASSERINI (N.). Composition of <i>Iris germanica</i> . Presence of Boron, Lithium, and Copper in the Plant	ii, 227
PICKELL (J. M.) and J. J. EARLE. Analyses of Oranges.	ii, 227
SESTINI (F.). Experiments with Wheat on the Substitution of Beryl- lium for Magnesium	ii, 228

	PAGE
MUNTZ (A.) and A. C. GIRARD. Loss of Nitrogen in Manures . . .	ii, 228
MAERCKER (M.). Effect of Phosphatic manuring on the Amount of Sugar and the Value of Beetroot . . .	ii, 228
MÜNTZ (A.) and H. COUDON. Ammoniacal Fermentation in Soils . . .	ii, 291
PETERMANN (A.). The Nitrogen Question . . .	ii, 291
BALLAND. Pre-existence of Gluten in Wheat . . .	ii, 292
OSBORNE (T. B.). Proteïds of Linseed . . .	ii, 292
TINSLEY (J. D.). Analyses of Kale, Turnip Salad, and Okra . . .	ii, 293
DUNNINGTON (F. P.) and T. C. WHITLOCK. Analysis of Black Earth . .	ii, 293
KARPLUS (J. P.). Production of Hydrogen Sulphide and Methyl Mer- captan by a Bacterium . . .	ii, 335
SCHLOSSING (T.), Jun., and E. LAURENT. Fixation of Free Nitrogen by Plants . . .	ii, 336
BOURQUELOT (E.). Occurrence of Trehalose in Fungi . . .	ii, 337
DEHÉRAIN (P. P.). Drainage Water from Arable Soils . . .	ii, 338
JENTYS (S.). Influence of Vegetation on the Pressure of Carbonic An- hydride in the Air of Soils . . .	ii, 341
BERTHELOT and ANDRÉ. The Organic Constituents of Soils . . .	ii, 341
PITSCH (O.). Are Nitrates Indispensable for the Growth of Plants? . .	ii, 385
BERTHELOT. The Nitrogen Fixing Micro-organisms . . .	ii, 429
DE CHALMOT (G.). Pentosans in Plants . . .	ii, 430
EWELL (E. E.) and H. W. WILEY. Products of Cassava . . .	ii, 430
PETERMANN (A.). Amount of Starch in different Varieties of Potatoes .	ii, 430
VINES (S. H.) and J. R. GREEN. Reserve Proteïd of the Asparagus Root	ii, 431
STAHL-SCHROEDER (M.). Reversion of Soluble Calcium Phosphate in Soil . . .	ii, 431
JÖRGENSEN (A.) and J. C. HOLM. Effront's Method for the Purification and Preservation of Yeast by means of Hydrofluoric acid . . .	ii, 481
LÉVY, (L.). Alcoholic Fermentation of Jerusalem Artichokes with Pure Yeast . . .	ii, 482
WINOGRADSKY (S.). Assimilation of Atmospheric Nitrogen by Microbes	ii, 482
BACH (A.). Assimilation of Carbonic Anhydride by Chlorophyllous Plants . . .	ii, 483
BACH (A.). Condensation of Carbonic Anhydride under the Influence of Sunlight . . .	ii, 484
MOLISCH (A.). Iron in Plants . . .	ii, 484
GIRARD (A.). Migration of the Starch of Potatoes in the Tubers . . .	ii, 485
JAHS (E.). Occurrence of Betaïne and Choline in Wormseed (<i>Arte- misia Gallica</i>) . . .	ii, 485
DEHÉRAIN (P. P.). Soil and Nitrification . . .	ii, 486
GODLEWSKI (E.). Nitrification . . .	ii, 544
HEBBRAND (A.). Changes in Mouldy Bread . . .	ii, 545
BITTÓ (B. v.). Composition of the Ripe Husks of Capsicum . . .	ii, 546
KINCH (E.). <i>Lathyrus sylvestris</i> . . .	ii, 547
CARPENTER (F. B.). Analysis of Tobacco cured by the Leaf-cure on Wire and by the Stalk Process . . .	ii, 547
PICHARD (P.). Greater Assimilability of the Nitrogen of recently formed Nitrates . . .	ii, 548
PETERMANN (A.) and J. GRAFTIAN. Combined Nitrogen in Rain . . .	ii, 548
STOKLASA (J.). Soluble Phosphoric acid in Superphosphate . . .	ii, 549
BEIJERINCK (M. W.). Butyl Alcoholic Fermentation and the Butylic Ferment . . .	ii, 586
NOBBE (F.) and L. HILTNER. How are Nodule-bearing Leguminosæ enabled to utilise Free Atmospheric Nitrogen? . . .	ii, 588
KOSSOVITCH (P.). Fixation of Nitrogen by Plants . . .	ii, 590
BRÉAL (E.). Assimilation of Nitrogen by Plants . . .	ii, 590
WEHMER (C.). Formation of Citric acid by the Fermentation of Glucose	ii, 591
COLBY (G. E.). Analysis of Californian Prunes, Apricots, Plums, and Nectarines . . .	ii, 591
JOHNSON (S. W.). Chemical Changes in Tobacco during Fermentation .	ii, 592

	PAGE
JOHNSON (S. W.). Analyses of Tobacco Stalks when cut and after curing	ii, 592
KILLGREN (A. G.) and L. F. NILSON. Swedish Fodder Plants	ii, 591
RHODIN (S.). Experiments with Ammonium Sulphate and Sodium Nitrate for Barley and Oats	ii, 593
EDLER. Manuring Potatoes	ii, 593
HARDIN (M. B.). Available Phosphoric acid and the Soluble Potash in Cotton Seed Meal	ii, 594

Analytical Chemistry.

LUNGE (G.). Improvements in Gasvolumeters.	ii, 41
KRAWCZYNSKI (S.). Titration Apparatus with Automatic Zero Adjustment	ii, 41
WAGNER (J.). Estimation of Free Acids in the presence of Acid Phosphates	ii, 41
NORTON (L. M.). Estimation of Chlorine in Electrolysed Solutions.	ii, 41
NIHOUL (E.). Estimation of Bromine and Iodine in presence of Chlorine	ii, 42
ALBERTI and HEMPEL. Estimation of Nitrogen in Nitrates	ii, 42
ULSCH (K.). Estimation of Nitrogen in Nitrates	ii, 42
GOOCH (F. A.) and H. W. GRUENER. Iodometric Estimation of Nitrates	ii, 42
REITMAIR (O.) and A. STUTZER. Estimation of Nitrous Acid in Sodium Nitrite	ii, 43
MULLER (J. A.). Estimation of Nitrogen in Soils by Kjeldahl's Method	ii, 43
WDOWISZEWSKI (H.). Estimation of Phosphorus in Steel	ii, 43
ZIMMERMANN (R.). Estimation of Phosphorus in Steel and Cast Iron	ii, 44
HANDY (J. O.). Rapid Estimation of Phosphorus in Iron, Steel, and Ores	ii, 44
MOREAU (B.). Precipitation of Phosphates and Arsenates by Ammonium Molybdate	ii, 45
LUNGE (G.) and L. MARCHLEWSKI. Estimation of Carbon in Iron or Steel, also of Carbonic Anhydride in Aqueous Solution	ii, 45
WENSE (W.). Estimation of Potassium as Perchlorate	ii, 46
JEAN (F.) and TRILAT. Estimation of Potassium	ii, 46
BIGGS (R. B.). Separation of Magnesium Chloride from the Chlorides of Sodium and Potassium	ii, 46
BROWNING (P. E.). Detection of Strontium in presence of Calcium	ii, 47
MAR (F. W.). Estimation of Barium in the presence of Calcium and Magnesium.	ii, 47
REGELSBERGER (F.). Assay of Aluminium and some of its Alloys	ii, 48
SCHONEIS (W.). Estimation of Aluminium in Steel, Bronze, &c.	ii, 49
MARCHAL (C.) and J. WIERNIK. Separation of Iron, Aluminium, and Chromium	ii, 49
RIHAN (J.). Colorimetric Estimation of Iron	ii, 50
L'HÔTE (L.). Estimation of Vanadium in Ores	ii, 50
DREHSCHMIDT (H.). Estimation of Cyanogen in Gas Refuse and in Illuminating Gas	ii, 50
MANGOLD (C.). Estimation of Glycerol	ii, 51
ALBERTI and HEMPEL. Estimation of Inorganic Constituents in Sugars	ii, 51
VOGEL (J. H.). Estimation of Sugar and Tannin in Wine	ii, 52
FLINT (E. R.) and B. TOLLENS. Estimation of Pentosans and Pentoses in Vegetables	ii, 52
PLANTA (A. V.) and E. SCHULZE. Estimation of Stachyose in the Tubers of <i>Stachys tuberosa</i>	ii, 53
PRIOR. Estimation of Acids in Beer	ii, 53
RAU (A.). Estimation of Succinic Acid	ii, 54

	PAGE
KLINGER (A.) and A. BUJARD. Estimation of Citric Acid in Wine . . .	ii, 54
GRAFFENBERGER (L.). Estimation of Milk Fat with Demichel's Lactobutyrometer . . .	ii, 55
MAYER (A.). Melting Point and Composition of Butter from Cows variously fed . . .	ii, 56
FAHRION (W.). Testing Linseed Oil Varnish . . .	ii, 56
REVERDIN (F.) and C. DE LA HARPE. Estimation of Aniline, Methyl-aniline, and Dimethylaniline . . .	ii, 56
HASELHOFF (A.). Analysis of Linseed Cake . . .	ii, 56
KLINGER (A.) and A. BUJARD. Detection of Cochineal in Sausages . .	ii, 56
BAUMANN (A.). Estimation of Hydrogen and Barium Peroxides . . .	ii, 56
KOSSLER (A.). Estimation of Hydrochloric Acid in the Contents of the Stomach . . .	ii, 56
BAUMANN (A.). Gas-volumetric Estimation of Iodine and Acids . . .	ii, 57
LUNGE (G.) and L. MARCHLEWSKI. Estimation of Nitric acid by its Specific Gravity . . .	ii, 57
ALBERTI and HEMPEL. Estimation of Nitrogen in Sodium Nitrite . .	ii, 57
GROSSMANN (J.). Estimation of Nitrites . . .	ii, 57
CHENEL (B. L.). Estimation of Nitrogen in Nitrates and Nitro-compounds by Kjeldahl's Method . . .	ii, 57
ARNOLD (C.) and K. WEDEMEYER. Kjeldahl's Method of estimating Nitrogen . . .	ii, 58
JOLLES (A. F.). Estimation of Phosphoric Acid in Basic Slag . . .	ii, 58
MANBY (C. E.). Estimation of Phosphorus . . .	ii, 59
TORREY (J.). Estimation of Sulphur in Slags . . .	ii, 59
GRITTNER (A.). Estimation of Sulphur in Coal . . .	ii, 59
CHERIX (C.). Volumetric Estimation of Sulphuric acid in Alkali Sulphates . . .	ii, 59
BAUMANN (A.). Estimation of Arsenious acid . . .	ii, 90
PAUL (T.). Estimation of Antimony and the Use of the Gooch Filter . .	ii, 90
BAUMANN (A.). Estimation of Antimonious Oxide . . .	ii, 90
BAUMANN (A.). Gas-volumetric Alkalimetry . . .	ii, 91
BLATTNER (N. G.). Estimation of Free Alkali in Commercial Hypochlorites . . .	ii, 91
MACLEROY (K. P.) and W. D. BIGELOW. Detection of Strontium in presence of Calcium . . .	ii, 92
GRITTNER (A.). Qualitative Separation of the Barium Group . . .	ii, 92
PROST (E.) and V. HASSEIDTER. Schaffner's Volumetric Zinc Process .	ii, 92
SPONHOLZ (E.). Volumetric Estimation of Thallium . . .	ii, 93
DROSSBACH (G. P.). Electrolytic Estimation of Copper . . .	ii, 93
RÜDORFF (F.). Quantitative Analysis by Electrolysis . . .	ii, 93
SCHMIDT (M.) and H. DFEYER. Separation and Estimation of Tin, Antimony, Lead, and Copper in Alloys . . .	ii, 95
SPONHOLZ (K.) and E. SPONHOLZ. Precipitation of Alumina in presence of Lithium . . .	ii, 95
DONATH (E.). Estimation of Aluminium in Ferro-aluminium . . .	ii, 96
ZIEGLER (A.). Analysis of Ferrosilicon, Ferroaluminium, Ferrotungsten, Ferrosilicon, and Ferrotitanium . . .	ii, 96
SMITH (E. F.). Electrolytic Separation of Platinum and Palladium from Iridium . . .	ii, 97
TSCHAPLOWITZ (F.). Estimation of Clay and Sand in Soils . . .	ii, 97
BAUMANN (A.). Gas-volumetric Estimation of Potassium Ferricyanide .	ii, 98
GUÉRIN (G.) and H. THORION. Ammonium Magnesium Urate . . .	ii, 99
WIECHMANN (F. G.). Estimation of a Mixture of Saccharose, Dextrose, and Lævulose . . .	ii, 99
SCHROEDER (M.). Estimation of Sugar in Cocoa Preparations . . .	ii, 100
SALKOWSKI (E.). Pentoses in Urine . . .	ii, 100
KOSSLER (A.) and E. PENNY. Volumetric Estimation of Phenol in Urine . . .	ii, 100
DEROIDE (E.). Estimation of Uric acid in Urine . . .	ii, 101

	PAGE
THÖRNER (W.). Estimation of Fat in Milk	ii, 101
AMTHOR (C.) and J. ZINK. Analysis of Lard	ii, 101
HÖNIG (M.) and G. SPITZ. Analysis of Mixtures of Saponifiable and Unsaponifiable Fats	ii, 102
FAHRION (W.). Hubl's Iodine Numbers	ii, 103
QUANTIN (H.). Analysis of Mixtures of Ammonia and Methylamines	ii, 104
HALLOPEAU (L. A.). Estimation of Peptone by Precipitation as Mercury Peptonate	ii, 104
BOENTRAEGER (A.). Use of Potassium Hydrogen Tartrate in Volumetric Analysis	ii, 144
MARCHLEWSKI (L.). Gas-volumetric Estimation of Iodine	ii, 144
BÖTTCHER (O.). Estimation of Nitrogen by Kjeldahl's Method	ii, 144
BÖTTCHER (O.). Estimation of Nitric Nitrogen	ii, 145
WINTON (A. L.). Modified Gunning-Kjeldahl Method for Use in presence of Nitrates	ii, 145
LILIENFELD (L.) and A. MONTI. Microchemical Localisation of Phosphorus in the Tissues	ii, 145
WEINIG (M.). Gravimetric Estimation of Sulphuric acid	ii, 145
LEHMANN (V.). Action of Benzoic Chloride on Ammonia	ii, 145
BÖDTKE (E.). Estimation of Urea	ii, 146
BARTHE (L.). Volumetric Estimation of Alkaloids	ii, 146
STUTZER (A.). Estimation of the Nitrogenous Constituents of Commercial Peptone	ii, 146
HERZBERG (W.). Detection of Resin in the Sizing of Paper	ii, 148
MANGOLD (C.). Analysis of Sealing Wax	ii, 148
FAHRION (W.). Testing Linseed Oil Varnish	ii, 148
FRIEDHEIM (C.) and R. J. MEYER. Quantitative Separation and Estimation of Chlorine, Bromine, and Iodine	ii, 183
JANNASCH (P.) and K. ASCHOFF. Direct Quantitative Separation of Chlorine and Iodine	ii, 183
ROBINEAU (F.) and G. ROLLIN. Detection of Iodates in Iodides	ii, 183
KEUSSLER (E. v.). Estimation of Nitrogen in Nitrocellulose	ii, 184
RUBTZOFF (P.). Estimation of Nitrogen in Organic Nitrates	ii, 184
LORENZ (N. v.). A Source of Error in the Estimation of Phosphoric Acid by Magnesia Mixture	ii, 185
SCHMIDT (F. W.). Can Arsenic be converted quantitatively into Hydrogen Arsenide?	ii, 186
NEHER (F.). Precipitation of Arsenic as Pentasulphide, and its Separation from Bismuth, Lead, Cadmium, and Antimony	ii, 186
MARCHLEWSKI (L. P.). Methods of estimating the Sulphur in Sulphides	ii, 186
LUNGE (G.). Estimation of Sulphur in Roasted Pyrites	ii, 187
HEMPEL (W.). Estimation of Sulphur in Coals and Organic Substances	ii, 187
STOLLE (E.). Volumetric Estimation of Sulphuric acid in Sulphates	ii, 188
RIPPER (M.). Estimation of Sulphurous acid in Wine	ii, 189
WENSE (W.). Estimation of Potassium as Perchlorate	ii, 190
VIZERN. Analysis of Hydrogen Alkali Carbonates	ii, 190
LOW (W. H.). Estimation of Free and Combined Alkali in Soap	ii, 191
WARWICK (H. S.). Electrolysis of Metallic Formates	ii, 191
ANTONY (U.) and L. NICCOLI. Separation of the Metals precipitated by Hydrogen Sulphide in Acid Solutions	ii, 192
MORAHT (H.). Titration of Ferric Salts	ii, 193
KARSLAKE (W. J.). Volumetric Estimation of Cobalt	ii, 194
PERRAULT (A.). Volumetric Estimation of Chromium	ii, 194
ROSENHEIM (A.) and C. FRIEDHEIM. Estimation of Vanadic Oxide	ii, 195
FRENKEL (M.). Palladium Compounds	ii, 195
GERHARD (F.). Estimation of Iron in Spring Water	ii, 196
BARILLOT (E.). Impurities in Crude Methyl Alcohol	ii, 196
SANFORD (P. G.). Analysis of Explosive Nitro-compounds	ii, 196

	PAGE
PARTHEIL (A.). Estimation of the Volatile Fatty Acids in Butter Fat . . .	ii, 197
VILLAVECCHIA (V.) and G. FABRIS. Baudouin's Test for Sesame Oil . . .	ii, 197
WEIBULL (M.). Estimation of Fat in Bread . . .	ii, 197
ANTUSHEVITCH (J. A.). Analysis of Bees-wax by Hübl's Method . . .	ii, 198
WILSON (J. A.). Estimation of Water and Free Fatty Matter in Soap . . .	ii, 198
SÜSS (P.). Estimation of Theobromine in Cacao Beans . . .	ii, 198
LÉGER (E.). Volumetric Estimation of Alkaloids . . .	ii, 199
PLUGGE (P. C.). Volumetric Estimation of Alkaloids . . .	ii, 199
BARTHE (L.). Analysis of Quinine Sulphate and Estimation of Quinine in presence of other Cinchona Alkaloids . . .	ii, 199
ROSENBACH (O.). Chromic acid as a Reagent for Albumin: Bile Pig- ments in Urine . . .	ii, 200
MULLER (J. A.). New Accessory to Lunge's Gas-volumeter . . .	ii, 229
MULLER (J. A.). New Gas-volumeter . . .	ii, 230
PARSONS (C. L.). Comparison of Methods for the Standardisation of Acid and Alkaline Solutions . . .	ii, 232
PARSONS (C. L.). Potassium Tetroxalate . . .	ii, 233
RIMBACH (E.). Employment of Borax for standardising Acids . . .	ii, 233
GRIGGI (G.). Detection of Hydrogen Peroxide . . .	ii, 233
SOLARO (A.). Estimation of Chlorine in Wine . . .	ii, 233
PAYNE (H. L.). Preparation of Standard Iodine Solution . . .	ii, 234
OST (H.). Estimation of Fluorine in the Ashes of Plants . . .	ii, 234
WINTON (A. L.). The Gunning-Kjeldahl Method, and a Modification applicable in the presence of Nitrates . . .	ii, 235
CAENOT (A.). Estimation of Phosphorus in Iron and Steel . . .	ii, 235
NEUBAUER (H.). Estimation of Phosphoric acid as Magnesium Pyro- phosphate . . .	ii, 236
BABBITT (H. C.). Precipitation of Ammonium Phosphomolybdate in the presence of Arsenic . . .	ii, 236
MAERCKER (M.). The Citrate and Molybdate Methods for the Estima- tion of Soluble Phosphoric acid . . .	ii, 237
MANCUSO-LIMA (G.). Estimation of Phosphoric Anhydride in Basic Slag . . .	ii, 238
MARTELLI (D.). Estimation of Phosphoric Anhydride in Basic Slag . . .	ii, 238
HUNDESHAGEN (F.). Eschka's Process for the Estimation of Sulphur . . .	ii, 239
VAN LEEUWEN (J. D.). Influence of the Sulphur contained in Coal Gas on the Estimation of Sulphur by Fusion . . .	ii, 239
RIPPER (M.). Gravimetric Estimation of Sulphuric acid . . .	ii, 239
ASBÓTH (A. v.). Volumetric Estimation of Sulphuric acid in Sulphates . . .	ii, 240
GILL (A. H.). Estimation of Carbonic Anhydride in the Air of Build- ings . . .	ii, 240
GOOCH (F. A.) and J. I. PHINNEY. Estimation of Rubidium by the Spectroscope . . .	ii, 240
HOLLEMAN (A. F.). Estimation of Calcium in Basic Slag . . .	ii, 241
BROWNING (P. E.). Quantitative Separation of Strontium and Calcium Nitrates by means of Amyl Alcohol . . .	ii, 241
BROWNING (P. E.). Quantitative Separation of Barium and Strontium by the Action of Amyl Alcohol on their Bromides . . .	ii, 241
TEED (F. L.). Detection and Estimation of Minute Quantities of Lead in the presence of Copper and Iron . . .	ii, 242
LUCKOW (C.). Volumetric Estimations and Separations by means of Potassium Ferrocyanide and Ferricyanide . . .	ii, 242
LUDWIG (E.). Detection of Mercury in the Organism . . .	ii, 243
ROZYCKI (P.). Estimation of Aluminium in Steel, Bronze, and Ferro- aluminium . . .	ii, 243
SACHSSE (R.) and A. BECKER. Behaviour of Ferric Oxide in Soil and Rocks . . .	ii, 243
ROSE (T. K.). Detection of Gold in Dilute Solutions . . .	ii, 245
VITALI (D.). Volumetric Estimation of Sulphates in Potable Waters . . .	ii, 245
MEINEKE (C.). Cyanogen Iodide and Sodium Thiosulphate . . .	ii, 246

	PAGE
MEINEKE (C.). Estimation of Cyanogen in Iodine	ii, 246
MEINEKE (C.). Detection of Cyanogen in Iodine	ii, 246
SALVATORI (S.). Oxidation of Glycerol in Acid Solution.	ii, 247
SALVATORI (S.). Estimation of Glycerol in Wine and other Fermented Liquids	ii, 248
DENIGÈS (G.). Metaphosphoric acid as a Precipitant of Proteïds in the Estimation of Sugar in Milk	ii, 248
GERRARD (A. W.). Estimation of Glucose	ii, 248
GUICHARD. Estimation of Starch	ii, 249
KLEEBERG (A.). Detection of Wheat Flour in Rye Flour	ii, 250
SUPINO (R.). Estimation of Acetone in Urine.	ii, 250
THÖRNER (W.). Estimation of Lactic acid in Milk	ii, 250
HEHNER (O.). Estimation of Oleïc acid	ii, 251
DE KONINGH (L.). Estimation of Oleïc acid	ii, 251
LASSAR-COHN. Estimation of Cholic acid in Bile	ii, 251
STOKES (A. W.). Estimation of Fat in Milk by Babcock's Method	ii, 251
SHUTT (F. T.). Babcock's Method of Milk Analysis.	ii, 251
RICHMOND (H. D.). Estimation of Total Solids in Milk.	ii, 252
PATTERSON (L. G.). Estimation of Butter Fat in Milk	ii, 252
ALLEN (A. H.). Volumetric Estimation of Alkaloids	ii, 252
RETGERS (J. W.). Use of Thallium Silver Nitrate for separating Minerals	ii, 294
AGLOT (E.). Estimation of Precipitates by an Optical Method	ii, 294
SALZER (T.). Normal Borax Solution	ii, 294
LÜTTKE (J.). Sensitive Litmus Indicator	ii, 294
KRÜSS (G.) and H. KRÜSS. Quantitative Spectrum Analysis	ii, 295
JANNASCH (P.) and K. ASCHOFF. New Direct Separation of Chlorine, Bromine, and Iodine.	ii, 295
EMICH (F.). Microchemical Detection of Sulphur	ii, 295
NEW (C. H.). Estimation of Nitrogen in Coal Gas	ii, 296
O'SULLIVAN (J.). Dumas' Method for estimating Nitrogen	ii, 297
STOCK (F. K.). Stock's Process for the Estimation of Nitrogen	ii, 297
GAMMARELLI (P.). Estimation of Nitric acid by means of Cinchonamine Salts	ii, 297
VAN DEVENTER (C. M.). Reaction of Nitrites and its Applications.	ii, 298
ARNOLD (C.) and K. WEDEMAYER. Spica's Process for the Estimation of Phosphoric acid	ii, 299
KNORRE (G. v.). Separation and Estimation of Pyrophosphoric and Metaphosphoric acids	ii, 299
BÄCKSTRÖM (H.). Estimation of Arsenic	ii, 299
ARCHBUTT (L.). Estimation of Silica in Clay	ii, 300
HILGARD (E. W.). Estimation of Potassium	ii, 300
DE KONINCK (L. L.). Detection of Ammonia with Nessler's Reagent	ii, 301
FRESENIUS (R.). Separation of Strontium and Calcium	ii, 301
COLEMAN (J. B.) and J. D. GRANGER. Volumetric Estimation of Calcium Phosphate by means of Uranium	ii, 301
KNIGHT (F. C.). Volumetric Estimation of Lead	ii, 302
LUNGE (G.) and E. SCHMID. Estimation of Oxygen in Lead	ii, 302
LOWE (W. F.). Gravimetric Estimation of Zinc as Sulphide	ii, 302
HINMAN (B. C.). Volumetric Estimation of Zinc	ii, 303
BORNTRÄGER (H.). Separation of Iron and Aluminium	ii, 304
REIS (M. A. v.). Estimation of Manganese in Iron	ii, 304
HOGG (T. W.). Analysis of Ferrosilicon and Siliceous Spiegel	ii, 304
WARREN (H. N.). Decomposition of Tin Slags by the Fluoride Method	ii, 305
RÜDORFF (F.). Quantitative Analysis by Electrolysis	ii, 305
SEYLER (C. A.). Supersaturation of Solutions of Oxygen in Water	ii, 306
JOHNSON (G. S.). Source of Error in the Ultimate Analysis of Organic Substances	ii, 306
MARPURGO (J.). Detection of Nitrobenzene	ii, 306
BÉHAL (A.) and C. CHOAY. Analysis of Creosotes	ii, 307

	PAGE
KUX (H.). Gas-volumetric Estimation of Organic Acids	ii, 307
RICHMOND (H. D.). The Reichert Process	ii, 307
CASSAL (C. E.). Estimation of Insoluble Fatty Acids	ii, 308
ALÉN (J. A.). Preservation of Milk for Analysis	ii, 308
RICHMOND (H. D.). Leffmann and Beam's Method for the Estimation of Milk Fat	ii, 308
LIEBERMANN (L.) and S. SZÉKELY. Estimation of Fat in Milk	ii, 308
GANTTER (F.). Iodine Absorption	ii, 309
LEWKOWITSCH (J.). Analysis of Fats	ii, 310
COLQUHOUN (W.). Estimation of Urea	ii, 310
SCHMIDT (J. H.). Estimation of Quinine in Cinchona Barks	ii, 310
CHIARMONTE (T.). Estimation of Tannin in Wine	ii, 311
STRUVE (H.). Chemico-legal Examination of Suspected Blood Stains	ii, 312
NIEBEL (W.). Detection of Horse Flesh in Food	ii, 312
LANDAUER (J.). The Origin of Blowpipe Analysis	ii, 342
FRIEDHEIM (C.) and H. LEO. Estimation of Acids by Calcium Carb- onate	ii, 342
KEBLER (L. F.). Detection of Chlorine, Bromine, and Iodine	ii, 343
MUTHMANN (W.) and J. SCHÄFFER. Estimation of Selenium	ii, 343
DEVARDA (A.). Direct Estimation of Nitrogen in Saltpetre	ii, 343
ARNOLD (C.) and K. WEDEMEYER. Estimation of Nitrogen in Urine	ii, 343
PETIT (A.) and L. MONFET. Estimation of Organic Nitrogen	ii, 343
VAN DEVENTER (C. M.). Gasometric Estimation of Nitrites by Schäffer's Reaction	ii, 344
FOERSTER (O.). Valuation of Basic Slags	ii, 344
HOLLEMANN (A. F.). Estimation of Potassium by the Lindo-Gladding Process	ii, 344
STONE (G. C.). Separation of Calcium and Magnesium from Zinc as Phosphates	ii, 344
HENRIQUES (R.). Estimation of Copper by Volhard's Thiocyanate Method	ii, 345
VIGNON (L.). Estimation of Mercury in Dilute Solutions of Mercuric Chloride	ii, 345
GLASER (C.). Separation of Iron Oxide from Alumina in Phosphatic Rocks by Fusion with an Alkali Carbonate	ii, 346
VAN DEVENTER (C. M.) and B. H. JÜRGENS. Investigation of Potable Water by Schäffer's Nitrite Reaction	ii, 346
BUCHNER (G.). Estimation of the Hardness of Water by means of Soap	ii, 347
JUMEAU (P. L.). Estimation of Ammonium Thiocyanate in Nitrogenous Manures	ii, 347
SOREL (E.). Distillation of Mixtures of Alcohol and Water	ii, 347
FERRIER (C.). Estimation of Sodium Sulphide, Sulphite, and Thiosulph- ate in Glycerol from Soap Works	ii, 348
SEESEN (J.). Detection of Small Quantities of Sugar in Urine	ii, 349
WIEDERHOLD (E.). Solubility of Rosin Oil and Mineral Oils and Mix- tures thereof in Acetone	ii, 350
RÖTTGER (H.). Qualitative and Quantitative Wax Analysis	ii, 351
BUCHNER (G.). Hübl's Process for Testing Wax	ii, 351
HELBING (H.) and F. W. PASSMORE. Detection of Foreign Fats in Wool Fat	ii, 351
MILLER (O.). Estimation of Indigotin in Commercial Indigo	ii, 352
SOKOLOFF (N. V.). Estimation of Theine in Tea	ii, 352
BEHREND (R.). Electrometric Analysis	ii, 387
HEMPEL (W.). Use of Sodium Peroxide in Analysis	ii, 387
ROSENBAUM (M.). Use of Chlorides, Hypochlorites, and Chlorates in presence of each other	ii, 388
GLADKY (P.). Estimation of Oxygen in Iron	ii, 388
SCHINDLER (W.). Estimation of Sulphur in Iron	ii, 389
STOKLASA (J.). Estimation of Nitrogen in Nitrates and in Nitric acid	ii, 389

MORGENSTERN and A. PAVLINOFF. Estimation of Phosphoric acid in Wines	ii, 389
HESS (W.). Analysis of Bone Meal, Fish Guano, and similar Phosphatic and Nitrogenous Manures	ii, 389
CASPARI (R.). Preparation of Perchloric acid and Estimation of Potassium in presence of Non-volatile Acids	ii, 390
WIERNIK (J.) and S. WIERNIK. Analysis of Crude Salt and Brines.	ii, 391
CLASSEN (A.). Quantitative Analysis by Electrolysis	ii, 391
RÜDORFF (F.). Electrolytic Analysis	ii, 391
JÜPTNER (H. v.). Estimation of Aluminium in Ferroaluminium	ii, 391
SCHNEIDER (L.). Steel Analysis	ii, 392
SYSSOYEFF. Gas-volumetric Analysis of Nickel	ii, 393
EMMENS (S. H.). Nickel Analysis	ii, 393
AUTENRIETH (W.). Potassium Ferrocyanide. Detection of Hydrocyanic acid in presence of Ferrocyanides	ii, 393
GOSSART (E.). Higher Alcohols and other Impurities in Ethyl Alcohol	ii, 393
SCHACHERL (G.). Estimation of Phenol in Crude Carbolic acid	ii, 394
HOPKINS (F. G.). Estimation of Uric acid	ii, 395
LÉGER (E.). Estimation of Benzoyl in Organic Compounds	ii, 395
HIRSCHSOHN (E.). Detection of Cineole in Ethereal Oils.	ii, 395
WEISS. Estimation of Fat in Milk	ii, 396
KREIS (H.). Modification of the Reichert-Meissl Method	ii, 396
SCHAFER. Goats' Milk and its Detection in Admixture with Cows' Milk	ii, 396
GRAFF (W.). Detection of Foreign Fats in Wool Fat	ii, 397
BENEDIKT (R.). Analysis of Bees-wax	ii, 397
STEIN (J.). Toxicological Reactions.	ii, 397
KELLER (C. C.). Estimation of Emetine in Ipecacuanha Root and in its Fluid Extract	ii, 397
ROSIN (H.). Detection of Bile Pigments in Urine	ii, 398
SEEGEN (J.). Precipitation of Proteids from Blood preparatory to the Estimation of Sugar	ii, 398
SPIEGLER (E.). Detection of Albumin in Urine	ii, 399
HENRIQUES (R.). Analysis of Rubber Goods	ii, 399
BREMER (G. J. W.). Apparatus for Extracting the Gases Dissolved in Water	ii, 432
BREMER (G. J. W.). Bottle for taking Samples of Water at Known Depths	ii, 432
BONDZYŃSKI (S.). Sjöqvist's Method of Estimating the Free Hydrochloric Acid in Gastric Juice	ii, 433
YOUNG (W. G.). Source of Error in the Volumetric Estimation of Chlorides by Mohr's Methods	ii, 433
HÖLAND (R.). Estimation of Sulphur in Organic Liquids	ii, 433
SCHMITT (T. F.). Estimation of Nitrogen in Nitrates	ii, 434
VILLIERS (A.) and F. BORG. Estimation of Phosphoric acid	ii, 434
MOISSAN (H.). Estimation of Boron	ii, 435
RUBRICUS (H.). Estimation of Silicon in Pig Iron	ii, 435
BREYER (T.) and H. SCHWEITZER. Estimation of Potassium by the Lindo Gladding Process	ii, 436
LOW (A. H.). Estimation of Alkalis in Silicates	ii, 436
FRESENIUS (R.). Separation of Barium, Strontium, and Calcium	ii, 436
JANNASCH (P.) and W. REMMLER. Quantitative Separation of the Metals of the Hydrogen Sulphide Group by means of Bromine Vapour	ii, 437
LOW (A. H.). Estimation of Lead	ii, 437
BONDZYŃSKI (S.). Detection of Mercury in Urine	ii, 438
LOW (A. H.). Estimation of Manganese in Ores	ii, 438
SCHULZE (H.). The Thiocyanate Test for Iron	ii, 438
NIHOUL (E.). Estimation of Iron by an Iodometric Method	ii, 439
TRILLAT (A.). Detection and Estimation of Formaldehyde	ii, 439

	PAGE
FAJANS (A.). Estimation of Salicylic Acid in presence of Phenols . . .	ii, 440
GANTER (F.). Detection and Approximate Estimation of Cotton-seed Oil in Lard and Olive Oil . . .	ii, 440
MÜLLER (M.). Distillation Apparatus for Analysis . . .	ii, 487
LE CHATELIER (H.). Estimation of Small Quantities of Combustible Gas mixed with Air . . .	ii, 487
FRIEDHEIM (C.). Volumetric Estimation of Free Chlorine . . .	ii, 488
LUNGE (G.) and F. BACHOFEN. Specific Gravity of Bleaching Powder Solutions . . .	ii, 488
GOOCH (F. A.) and P. E. BROWNING. Estimation of Iodine in Haloid Salts by the Action of Arsenic acid . . .	ii, 488
MESLANS (M.). Estimation of Fluorine in Combustible Gases . . .	ii, 488
CARNOT (A.). Estimation of Phosphorus in Soil . . .	ii, 489
NEUBAUER (H.). Estimation of Phosphoric acid as Magnesium Pyrophosphate . . .	ii, 489
HOLLEMAN (A. F.). Volumetric Estimation of Phosphoric acid . . .	ii, 490
REISCHLE (A. K.). Estimation of Boric acid . . .	ii, 491
GLINKA (F.). Analysis of Silicates by Deville's Method . . .	ii, 491
PETTERSSON (O.) and A. SMETT. Estimation of Carbon in Iron and Steel . . .	ii, 491
LORENZ (R.). Estimation of Carbon in Steel . . .	ii, 491
JEAN (F.). Volumetric Estimation of Copper, Iron, Antimony, and Zinc in Zinc Powder . . .	ii, 492
JANNASCH (P.). Separation of Metals in Alkaline Solution by Hydrogen Peroxide . . .	ii, 492
JANNASCH (P.). Separation of Lead from Silver in Ammoniacal Solution by means of Chromic acid . . .	ii, 493
JEAN (F.). Analysis of Impure Galena: Estimation of Copper and Zinc . . .	ii, 493
HANNAY (J. B.). Analysis of Pigments Ground in Oil . . .	ii, 494
HARLAND (R. H.). Analysis of Ground White Lead . . .	ii, 494
CLASSEN (A.). Quantitative Analysis by Electrolysis . . .	ii, 495
SMITH (E. F.) and J. C. SALTAR. Electrolytic Separation of Metals . . .	ii, 495
CLASSEN (A.). Separation of Copper from Bismuth . . .	ii, 495
SMITH (E. F.) and D. L. WALLACE. Electrolytic Separation of Copper from Antimony . . .	ii, 495
LABORDE (J.). Volumetric Estimation of Mercury . . .	ii, 495
SMITH (E. F.) and J. B. MOYER. Electrolytical Separation of Mercury from Bismuth . . .	ii, 496
SMITH (E. F.) and J. B. MOYER. Electrolytic Separations . . .	ii, 496
CARNOT (A.). Estimation of Manganese Oxides by means of Hydrogen Peroxide . . .	ii, 497
CARNOT (A.). Estimation of Manganese by Oxydometric Methods . . .	ii, 497
JEAN (F.). Estimation of Manganese in Minerals . . .	ii, 498
WIECHMANN (F. G.). Estimation of Iron and Aluminium in Bone Black . . .	ii, 498
MAHON (R. W.). Modification of the Stannous Chloride Method of titrating Iron . . .	ii, 499
PARRY (J.) and J. J. MORGAN. Analysis of Iron and Steel . . .	ii, 499
KNORRE (G. v.). Separation of Nickel and Cobalt by means of Nitro- β -naphthol . . .	ii, 500
JANNASCH (P.) and J. MAI. Quantitative Separations in presence of Hydroxylamine . . .	ii, 500
MOORE (T.). Assay of Tin Ore . . .	ii, 501
KLINGEMANN (F.). Method for the Simultaneous Estimation of Carbon and Nitrogen in Organic Compounds . . .	ii, 501
MAROUBY. Detection of Adulteration in Wines . . .	ii, 501
MULLER (J. A.). Estimation of the Dry Residue in Wines . . .	ii, 501
DENIGÈS (G.). Identification and Estimation of the Lactoses in different Milks . . .	ii, 502
GUICHARD. Polarimetric Examination of Gums . . .	ii, 502
LOPES (S.). Detection of Hydrocyanic acid . . .	ii, 502

	PAGE
JUMEAU (P. L.). Estimation of Thiocyanic, Hydrocyanic, and Hydrochloric acids	ii, 503
SCHNEEGANS (A.) and J. E. GEROCK. Detection of Free Salicylic acid in Salicylaldehyde and Methylsalicylic acid	ii, 503
VEDRÖDI (V.). Analysis of Tobacco	ii, 504
GANTTER (F.). Detection of Saccharin in Beer	ii, 504
NEITZEL (E.). Titration of Acids by Metallic Sodium	ii, 550
FAIRLEY (T.). Estimation of Chlorine in Water	ii, 550
GRUENER (H.). Iodometric Estimation of Nitrates	ii, 550
WEDEMAYER (K.). Estimation of Nitrates by Schmitt's Method	ii, 551
MARCHLEWSKI (L.). Methods of estimating Sulphur	ii, 551
PHINNEY (J. I.). Treatment of Barium Sulphate in Analysis	ii, 552
BROWNING (P. E.). Influence of Nitric acid and Nitro-hydrochloric acid on the Precipitation of Barium Sulphate	ii, 552
BABBITT (H. C.). Emmerton's Process for the Estimation of Phosphorus	ii, 553
NASTIUKOFF (A.). Colorimetric Analyses of Phosphorites	ii, 553
DUDLEY (C. B.) and F. N. PEARSE. Estimation of Phosphorus in Steel	ii, 553
CAMPBELL (E. D.). Estimation of Phosphorus in Iron in presence of Arsenic	ii, 554
VILLIERS (A.) and F. BORG. Estimation of Potassium	ii, 554
WELLS (H. L.). Quantitative Separation of Cæsium	ii, 554
LENOBLE (E.). A Reaction of Cupric Salts	ii, 554
GYÖRY (S.). Volumetric Estimation of Arsenic and Antimony	ii, 554
GEORGIS (G.). Estimation of Chromium in Products of the Iron Industry	ii, 554
BRUTTINI (A.). Colorimetric Estimation of Small Quantities of Uranium in Minerals	ii, 555
CALDWELL (G. C.). Estimation of Sugar in Tomatoes	ii, 555
LAVES (E.). Detection and Estimation of Glucose by means of Phenylhydrazine	ii, 555
KRUG (W. H.). Gravimetric Estimation of Furfuralhydrazone	ii, 556
ROBINEAU (F.) and G. ROLLIN. Volumetric Estimation of Acetone	ii, 556
OFFERMANN (H.). Detection and Estimation of Thiocyanates in Ammonium Sulphate	ii, 556
RAU (A.). Estimation of Succinic acid	ii, 557
BUCKET (M.). Examination of Tartaric and Citric acids for Lead	ii, 557
ORDONNEAU (C.). Calcium Tartrate from Distillery Residues; its Estimation and Purification	ii, 558
KREIDL (I.). Estimation of Uric acid	ii, 558
KINNEAR (J. B.). Estimation of Solids and Fat in Milk	ii, 559
LIDOFF (A.). The Elaidin Reaction	ii, 559
GRANDVAL (A.) and H. LAJOUX. Estimation of Caffëine	ii, 559
KOTTMAYER (G.). Estimation of Emetine in Ipecacuanha Root	ii, 560
BENEDIKT (R.) and H. STRACHE. Analyses of Ethereal Oils	ii, 560
CAMERER (W.). Hüfner's Method of estimating Urea	ii, 560
VOGEL (O.). The Oxy-Coal Gas Flame for Spectrum Analysis	ii, 594
JANNASCH (P.) and K. ASCHOFF. Separation of Iodine, Bromine, and Chlorine. Estimation of Bromine in Mineral Waters, &c.	ii, 595
ROBERTS (C. F.). Reduction of Nitric acid by Ferrous Salts	ii, 595
ROBERTS (C. F.). Estimation of Chlorates and Nitrates, and of Nitrates and Nitrites in one Operation	ii, 596
MACFARLANE (W.) and A. WILSON. Rapid Estimation of Phosphorus in Iron and Steel	ii, 596
WAVELET (C.). Volumetric Estimation of Phosphates	ii, 597
FAVREL (G.). Volumetric Estimation of Pyrophosphoric acid and Alkali Pyrophosphates	ii, 597
FAVREL (G.). Volumetric Estimation of Alkalis in Arsenites	ii, 598
GARNIER (M.). Toxicological Examination for Metals	ii, 598
BAYER (A.). Direct Estimation of Potassium and Sodium by means of Tartaric acid	ii, 598

	PAGE
ALEXANDER. Volumetric Estimation of Lead	ii, 599
WARINGTON (R.). Detection and Estimation of Lead in Tartaric and Citric acids.	ii, 599
FRANKEL (L. K.). Detection of Lead in Urine	ii, 600
KOSMANN (B.). Separation of Iron, Aluminium, Manganese, Zinc, and Calcium	ii, 600
GARNIER (L.). Separation of Arsenic and Antimony	ii, 600
GRUENER (H.). Stability of Standard Solutions of Tartar Emetic	ii, 600
DAFERT (F. W.). Estimation of Nitrogen in Soils	ii, 601
NIHOUL (E.). Estimation of Sugars by means of Fehling's Solution	ii, 601
BAU (A.). Estimation of Isomaltose in Worts	ii, 601
PFLÜGER (E.). Estimation of Glycogen	ii, 601
WEISS. Estimation of Fat in Milk	ii, 601
LAVES (E.). Analysis of Butter	ii, 602
RIDEAL (S.). Sulphuric Acid Hydrolysis of Butter-Fat	ii, 602
GANNTER (F.). Discrimination of Butter from Margarin	ii, 603
CROOK (W. G.). Detection of Heated Cotton Seed Oil in Lard	ii, 603
SMETHAM (A.). Rapid Saponification of Oils	ii, 603
FAHRION (W.). Analysis of Oils	ii, 603
FAHRION (W.). A New Method of Milk Analysis	ii, 604
KLIMONT (J.). Detection and Estimation of Neutral Fats in Mineral Oil	ii, 604
REINHARDT (H.). Analysis of Aniline Oils	ii, 605
VAUBEL (W.). Assay of Alkylanilines	ii, 605
PETERSEN (J.). Estimation of Hydrazine in Hydrazine Salts	ii, 605
LINDEMAN and MOTTEU. Detection of Alkaloids, "Saccharin," and Salicylic acid	ii, 606
VITALI (D.). Volumetric Estimation of the Alkaloids and of some Metals.	ii, 606
CANNEPIN and VAN EIJK. Titration of Morphine	ii, 607
HEUT (G.). Conine and Nicotine	ii, 607
GUILLLOT. Rapid Estimation of Caffeine in Tea and Coffee	ii, 608
BRUNNER (H.) and H. LEINS. Separation of Theobromine and Caffeine	ii, 608
GRANDVAL (A.) and H. LAJOUX. Estimation of Alkaloids	ii, 608
LEWKOWITSCH (J.). Estimation of Resin in Soaps	ii, 609
GREEN (A. G.). Qualitative Analysis of Coal Tar Colouring Matters	ii, 610
BENNO-LAQUER. Albumin and Sugar in Urine	ii, 610
GANNTER (F.). Valuation of Hide Clippings for Glue-making	ii, 610
DYER (B.) and J. F. H. GILBARD. Discrimination between Genuine and Exhausted Ginger	ii, 611
THÖRNER (W.). Estimation of Fibre in Foods by aid of the Centrifugal Machine	ii, 611
RICHARDSON (F. W.). Estimation of Silks in Fabrics	ii, 611

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Refractometric Observations. By J. F. EYKMAN (*Ber.*, **25**, 3069—3079).—The author has determined the refraction and dispersion equivalents of a considerable number of isomerides with a view of drawing conclusions as to their constitution from the values of their molecular constants. The measurements were made for the lines H_β and H_α . His results for the molecular refraction and dispersion calculated by means of Gladstone's and of Lorenz's formulæ are given in the following table:—

	Molecular refraction for A.		Molecular dispersion from H_β and H_α .	
	Gladstone.	Lorenz.	Gladstone.	Lorenz.
Piperidine, $C_5H_{11}N$	43·42	26·01	0·87	0·45
$C_6H_{13}N$.				
1. Methylpiperidine	51·50	30·96	1·10	0·57
2. Methyl- α -methylpyrrolidine	51·24	30·89	1·09	0·56
3. $\alpha\alpha_1$ -(2, 5) Dimethylpyrrol- idine (Tafel)	50·97	30·70	1·01	0·53
4. Butallylmethylcarbinamine	52·99	31·92	1·20	0·63

	Molecular refraction for A.		Molecular dispersion from H_β and H_α .	
	Gladstone.	Lorenz.	Gladstone.	Lorenz.
$C_7H_{15}N$.				
1. Methyl- α -pipercoline—				
(a.) From pentallylcarbini- methylamine	58·74	35·28	1·24	0·65
(b.) From Ladenburg's pipe- coline.....	58·62	35·18	1·24	0·64
2. Methyl- $\alpha\alpha_1$ -dimethylpyrrol- idine	58·63	35·30	1·21	0·63
3. Dimethylpiperidine	60·71	36·68	1·41	0·74
$C_8H_{17}N$.				
1. Pentallylcarbini-dimethyl- amine	68·40	41·26	1·58	0·82
2. Butallylmethylcarbini- methylamine	68·01	40·99	1·51	0·80
$C_9H_{15}N$.				
1. α -Methyltropidine	73·23	43·29	2·27	1·13
2. β -Methyltropidine	75·79	44·39	2·54	1·23
C_6H_{10} .				
(a.) Diallyl (b. p. 60—61°).	46·33	28·08	1·26	0·67
(b.) „ (b. p. 80—83°).	47·85	28·72	1·80	0·92
Tropilidene, C_7H_8	51·50	30·32	2·06	1·00
Tropilen, $C_7H_{10}O$	53·05	31·45	1·46	0·72
Tropidine, $C_8H_{13}N$	61·73	36·59	1·41	0·71
Tropine, $C_8H_{15}NO$	64·62	38·29	1·18	0·60
Ecgonine, $C_9H_{15}NO_3 \cdot H_2O$	79·90	46·44	1·56	0·75
Pseudotropine (= Oscine)—				
(a.) Calc. for $C_8H_{15}NO$ (Ladenburg)	58·49	34·91	1·05	0·46
(b.) Calc. for $C_8H_{13}NO_2$ (Hesse, Schmidt)....	64·30	38·38	1·16	0·50
Acetylacetone, $C_6H_{10}O_2$...	48·91	29·51	0·97	0·51

These results the author discusses in reference to the probable constitution of the substances, and finds that they agree in general with the views expressed by Merling (Abstr., 1891, 1506), from whom most of the specimens examined were obtained. J. W.

Physical Character of the Lines in the Spark Spectra of the Elements. By W. N. HARTLEY (*Proc. Roy. Soc.*, 49, 448—451).—Perrot has shown that the spark discharge is composed of two parts: the fiery track or central portion is a statical discharge, whilst the aureole or flame is dynamic and capable of electrolytic action.

From observations of the sparks and photographs of the spectra, the author considers that the principal lines lying between point and point of the electrodes are spectra of the fiery path of the spark; the extension of the principal lines above and below the points of the electrodes seem to be spectra of the aureole. Elements which are difficultly volatile, and those which are bad conductors, do not exhibit

spectra with extended lines, and, conversely, metals which are the best conductors, and the most volatile, give spectra with their principal lines largely extended. The metals magnesium, zinc, cadmium, aluminium, indium, copper, silver, and mercury are the best conductors, and consequently show considerable extension of their principal lines. With these metals, the continuous spectrum is very weak, and in the cases of thallium and mercury, the air spectra are suppressed by the dense vapours in the track of the spark. The extension of the lines is even observed with concentrated solutions of the metals.

The nimbus seems not to be wholly dependent on the volatility or readiness with which the metal is oxidised, although volatility certainly increases the nimbus. Amongst the photographed spectra, that of magnesium shows the largest nimbus, owing probably to the great actinic power of the rays emitted, and also to the large quantity of the metal in the track of the spark. After magnesium, cadmium and mercury exhibit the largest nimbus; those of platinum, gold, copper, and silver are small. There is a considerable nimbus about some of the lines of arsenic, antimony, bismuth, tin, and lead, and but very little about those of thallium and iridium. The nimbus is evidently an expression of the quantity of matter in the spark, and of the chemical activity of the rays emitted by the ignited vapour.

The continuous spectrum, which forms the background to the lines of certain spectra, must be due to the ignition of some solid substance or oxide. The spectra of gold, silver, platinum, mercury, iridium, zinc, and cadmium, metals which either are not oxidisable or form volatile oxides, do not have this background; the less metallic elements, tellurium, arsenic, antimony, and bismuth, however, show it very strongly. No sufficient explanation of this has yet been given.

The breadth of the principal lines in the photographed spectra is dependent on the actinic power, volatility, vapour density, and electrical conductivity of the metal. In accordance with this, the lines of cadmium are broader than those of zinc, which are in turn broader than those of magnesium.

W. J. P.

The Planté Lead | Sulphuric Acid | Lead Peroxide Cell from a Chemical Standpoint. Part I. By G. H. ROBERTSON (*Proc. Roy. Soc.*, 50, 105—108).—The author was unable, either directly or indirectly, to obtain any evidence of the existence of an oxysulphate of lead corresponding with red lead; there is, therefore, no ground for supposing that the ordinary lead sulphate is not the only one concerned in the reactions occurring in the Planté cell. If the sudden lowering of the E.M.F. were caused by a change in the nature of the chemical compounds formed on the plates, it would be difficult to account for the very rapid recovery of the E.M.F. exhibited by an apparently discharged cell.

It would seem that the different behaviour of secondary cells containing sodium sulphate (1 per cent.) and cells containing none is due to the catalytic action of this salt on the hydrogen peroxide always found in the electrolysed acid of the strength used in such batteries, which is probably formed from persulphuric acid. Cells containing sodium sulphate show much less sulphating than do

ordinary cells, and the addition of this salt (1 per cent.) to the freshly electrolysed acid is always attended by a diminution in the amount of hydrogen peroxide. The acid taken from secondary cells reduces lead dioxide, and if hydrogen peroxide be added to the acid in the cells, an annulment or reversal of the E.M.F. occurs, whilst the introduction of hydrogen peroxide into the body of the dioxide paste produces an increase of E.M.F. in the case of a platinum | lead dioxide couple. The pink colour assumed by the acid in the Planté cell is due to the formation of permanganic acid from impurities in the lead.

W. J. P.

The Planté Lead | Sulphuric Acid | Lead Peroxide Cell from a Chemical Standpoint. Part II. Discussion of the Chemical Changes occurring in the Cell. By H. E. ARMSTRONG and G. H. ROBERTSON (*Proc. Roy. Soc.*, **50**, 108).—The authors arrive at the following conclusions:—(1.) That the cooling observed in the Planté cell can only be explained as resulting from the dissociation of the dilute sulphuric acid. (2.) That the observed loss in efficiency cannot be due to temperature changes, as these arise through actions occurring out of circuit. (3.) That if sulphating occurs at both plates in circuit and under the influence of sulphuric acid, the calculated E.M.F. is considerably higher than the observed value, whilst, if sulphating occur only at the lead plate, the calculated E.M.F. is far too low. This comparison, therefore, leads to no conclusion as to the exact nature of the changes which take place in the cell. (4.) That a counter E.M.F. of about 0.5 volt would account for the observed departure from the highest calculated value. Such a counter E.M.F. may exist, peroxides being always present in the electrolyte. (5.) That the observed loss of efficiency is due to the formation of peroxides in the electrolyte, and to the excessive sulphating occurring chiefly at the dioxide plate in the local circuit existing between the support and the paste.

W. J. P.

Electrolysis of Silver Nitrate in a Vacuum. By A. SCHUSTER and A. W. CROSSLEY (*Proc. Roy. Soc.*, **50**, 344—358).—The deposit of metallic silver obtained on electrolysis of silver nitrate solution in air, increases slightly in weight as the current density at the platinum cathode decreases. The authors find that this difference is persistent when the deposition occurs in a vacuum. The deposit is slightly increased in weight if electrolysis proceeds under diminished pressure; this is due to the withdrawal of oxygen, for if the solution be electrolysed in an atmosphere of this gas, a heavier deposit is obtained than in air.

The authors conclude that the true electrochemical equivalent of silver is probably not quite 0.1 per cent. greater than the value assigned to it by Rayleigh.

W. J. P.

Electrolytic Dissociation and Ionisation. By J. TRAUBE (*Ber.*, **25**, 2989—2993; compare *Abstr.*, 1891, 255, 390, 638).—The author now practically adopts the hypothesis of electrolytic dissociation to explain the behaviour of aqueous salt solutions, contending, however, that the dissociation into ions need not be complete dis-

sociation, but only a slackening of the bonds which hold the ions together. This modified dissociation he calls, after Fitzgerald, ionisation.

J. W.

Absorption of Radiant Heat by Alum. By C. C. HUTCHINS (*Amer. J. Sci.* [3], 43, 526).—It is a generally accepted opinion that a solution of alum acts as a particularly efficient absorber of rays of great wave-length; but the author shows by direct experiment that a solution of alum is really no better absorber than water, and that, furthermore, it would hardly pay to use plates of transparent alum, even if they were to be had.

H. C.

Specific Heat of Carbonic Anhydride. By N. S. KURNAKOFF (*J. Russ. Chem. Soc.*, 22, 493—495).—From the apparent specific heat of carbonic anhydride at high temperatures (above 2000°) the author calculates the true specific heat by means of the formula $c = \frac{Ct - k(W + c_1t)}{(1 - k)t}$, in which c is the true specific heat of carbonic anhydride, C the apparent specific heat, c_1 the mean specific heat of its products of dissociation (carbonic oxide and oxygen), W the heat of formation of carbonic anhydride from its dissociation products at 0°, k the coefficient of dissociation, and t the temperature. The following table of results is given by the author. In it, the values of c_1 are taken from Vielle's data, and the values of k are those given by Le Chatelier. $W = 68,000$ cal.

t .	C .	c_1 .	k .	c .
2000°	19·1	9·0	0·035	18·3
2500	19·8	9·2	0·14	17·1
3000	20·6	9·4	0·3	15·7
3500	21·3	10·6	0·4	15·5
4000	22·1	11·5	0·45	17·0
4500	22·8	12·3	0·6 (?)	16·0

The true specific heat would thus seem to reach a minimum value at about 3500°.

J. W.

Heat of Combustion of Chlorine Compounds. By BERTHELOT and MATIGNON (*Compt. rend.*, 115, 347—350).—

	Heat of combustion. Const. vol.	Molecular heat of combustion.		Heat of formation.
		Const. vol.	Const. press.	
Chloracetic acid	—	+174·2 cal.	+173·9 cal.	+123·0 cal.
Trichloracetic acid	—	+106·3 „	+105·4 „	+132·1 „
Dichlorotrimethylene ...	3900 cal.	+432·8 „	+433·1 „	-2·6 „

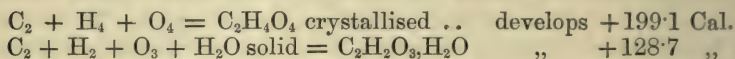
The substitution of chlorine for hydrogen in acetic acid develops +25.3 Cal.; the substitution of 3 atoms of chlorine for 3 atoms of hydrogen in acetic acid develops +26.1 \times 3 Cal. These numbers are somewhat lower than in the case of the substitution of chlorine for hydrogen in methane, the difference being probably due to the presence of oxygen.

The substitution of 2 atoms of chlorine for hydrogen in trimethylene develops +34 - x Cal., x being the heat of formation of the hydrocarbon.

C. H. B.

Glyoxylic or Dihydroxyacetic Acid. By BERTHELOT and MATIGNON (*Compt. rend.*, 115, 350—353).—The experiments were made with a crystallised specimen of glyoxylic acid which had lost 0.213 mol. H_2O , and the final values were calculated on the assumption that recombination with this quantity of water would cause no thermal disturbance.

Heat of combustion of glyoxylic acid at const. vol. = +128.1 Cal., at const. press. 127.5 Cal., and consequently



The conversion of ethane into gaseous alcohol by direct oxidation would develop +34.6 Cal.; the oxidation of alcohol to aldehyde develops +51.5 Cal., and of aldehyde into acetic acid +60.0 Cal. For the corresponding values in the cases of acetic, glycollic, and glyoxylic acids see following abstract.

As a rule, the substitution of HO for H in an acid, with production of an alcoholic function, develops from +35 to +45 Cal.

C. H. B.

Heat of Combustion of Glycollic Acid. By BERTHELOT (*Compt. rend.*, 115, 393).—Stohmann points out that the heat of combustion of glycollic acid as determined by Louguinine (*Ann. Chim. Phys.* [6], 23, 210—213) is +166.0 Cal., and not +186.0 Cal. It follows that the conversion of acetic acid into glycollic acid would develop +40.2 Cal., and the conversion of acetic acid into glyoxylic acid would develop +79.4 Cal. or +39.7 \times 2.

C. H. B.

Thermochemistry of Carbon Compounds of Mixed Function. By L. VIGNON (*Compt. rend.*, 115, 354—356).—Experiments

	Heat of dissolution.	Heat developed by		
		1 mol. HCl.	2 mols. HCl.	3 mols. HCl.
$\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2 \dots\dots$	+0.06 Cal.	+3.50	+2.35	+0.61
$\text{CO}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2 \dots\dots$	+0.26 „	+0.87	+0.00	+0.00
$\text{CS}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2 \dots\dots$	+0.22 „	+1.35	—	—

were made with tetramethyldiamidodiphenylmethane, tetramethyldiamidobenzophenone, and tetramethyldiamidothiobenzophenone.

The presence of the ketonic group CO destroys the basic function, but this effect is only partial in the case of the thioketonic group CS
C. H. B.

Specific Gravity of Ice. By J. V. ZAKRZEWSKI (*Ann. Phys. Chem.* [2], 47, 155—162).—It is pointed out by the author that the determinations of the specific gravity of ice at the freezing point are not sufficiently accurate for the purposes of exact heat measurement by means of Bunsen's ice calorimeter. By using a modification of this instrument, he has made fresh determinations of the specific gravity of ice at temperatures very near 0°. The calorimeter was filled with mercury and boiled-out water, the exact weight of which was ascertained. This water was frozen very slowly at a temperature just below the freezing point, the crystallisation being started at a given point by means of the external application of solid carbonic anhydride and ether. The mercury expelled was then weighed. A check determination was made by melting the ice and ascertaining the weight of mercury sucked up by the apparatus. The two weights usually differed by a few milligrams on a total of 15—30 grams. The results of the measurements are as follows:—

Temperature.	Specific gravity.
—0·705°	0·916710
—0·700°	0·916713
—0·699°	0·916708
—4·720°	0·916995

From these values, the specific gravity of ice at 0° is 0·916660, and the coefficient of expansion 0·000077.
J. W.

Relation between the Specific Gravity of Acid or Saline Solutions and the Molecular Weight of the Dissolved Substances. By A. DE SAPORTA (*Bull. Soc. Chim.* [3], 7, 184—190).—An acid or saline solution made by dissolving 52·63 grams of substance in a litre of distilled water is termed a *typical solution*, and is usually of greater sp. gr. than water. The excess of the sp. gr. above unity is termed the *typical density A* (*alourdissement type*), and if a gram-molecule *P* of the substance is substituted for the constant amount, a quantity $AP/52·63$ is obtained which is termed the *theoretical molecular density*, and is held to be proportional to the *molecular excess* or difference between the molecular weight of the dissolved substance and that of water, $AP/52·63 = K(P - 18)$. From this it follows that $A/K = 52·63 - 947·34/P$, and the truth of the above supposition can be tested by comparing the values calculated from the right-hand side of the equation with those calculated from the left-hand side. The results are given for most of the commonly occurring inorganic acids and salts, and the agreement is fair, as a rule, when *K* is taken as unity, although more consistent results are obtained in some cases by giving it a higher value.
JN. W.

Specific Volume of Sulphur. By M. TOEPLER (*Ann. Phys. Chem.* [2], 47, 169—174).—Monoclinic sulphur, plastic sulphur, obtained by rapid cooling from 140—170° to 20°, and liquid (syropy) sulphur, obtained by very slow cooling through the same range of temperature, have been investigated by the author with respect to the volume they occupy at different temperatures.

His results are contained in the following table, the volume of liquid sulphur at 120° being taken as unity:—

	Monoclinic.	Liquid.	Plastic.
—20°	—	0·935	—
0	0·915	0·943	—
20	0·919	0·951	—
40	0·924	0·960	0·974
60	0·929	0·969	0·979
80	0·935	0·979	—
100	0·941	0·9889	—
120	—	1·0000	0·995
140	—	1·0117	1·001
160	—	—	1·007
180	—	—	1·014
200	—	—	1·021

J. W.

Relations between the Surface Tensions of Liquids and their Chemical Constitution. By C. E. LINEBARGER (*Amer. J. Sci.* [3], 44, 83—92).—The author points out that up to the present little or nothing has been done towards establishing relations between the surface tensions of liquids and their chemical constitution. He proposes to investigate the subject, and the present paper is devoted mainly to a description of the method to be used in carrying out the experiments. This consists in determining the number of drops into which a certain volume of water divides in dropping down through liquids lighter than water, and in dropping up through liquids heavier than water, and the number of drops of a liquid dropping down, if heavier than water, and dropping up, if lighter, through that standard.

At the surface of two absolutely insoluble liquids, there would reign complete repulsion between the molecules; no molecule of one liquid would pass beyond a definite surface concentric with the surface of the liquids, and this surface would form an impenetrable barrier to molecules of each liquid. But in the case of liquids which dissolve one another a little, complete repulsion between the molecules prevails no longer, but, on the contrary, a slight attraction, so that now a molecule of one liquid may pass into the other. This would continue until the tension of solution of each liquid was reached. The question arises, whether the superficial tensions of liquids, saturated with each other, or pure, should be employed. In this preliminary investigation only the superficial tensions of liquids uncontaminated with one another were determined.

The experiments recorded with hydrocarbons and their derivatives indicate clearly that a connection exists between surface tension and

chemical constitution, but the data obtained are not yet sufficient to admit of generalisations being made. The author is continuing these investigations.

H. C.

Tensions of Vapours. By C. ANTOINE (*Ann. Chim. Phys.* [6], **22**, 281—288).—In former papers (*Compt. rend.*, **107**, 681, 778, 836), the author has shown that the tensions of vapours could be calculated by the formula $\log H = A - \frac{B}{t + c}$; the object of this communication is simply to modify some of the coefficients previously given, and to show how far the calculated values agree with those determined experimentally.

F. S. K.

Elasticity of Gases. By C. PUSCHL (*Monatsh.*, **13**, 635—646).—Mendeléeff and others have shown that the product pv , which, in general, decreases on compression and increases on expansion, behaves in a precisely opposite manner at low pressures, and on expansion this product, therefore, reaches a maximum and then decreases. On the other hand, the fact that on compression the product reaches a minimum and then increases is well known. It follows from this that there are, ordinarily speaking, two points at which any gas will exactly obey Boyle's law. From experiments of Witkowski and others, it can be shown that the maximum of pv occurs with rising temperature at higher and higher pressures; the minimum, on the other hand, occurring at lower and lower pressures as the temperature rises. It, therefore, follows that at some particular temperature the above pressures for maximum and minimum pv will become the same, and the two points coincide. The point at which this occurs may be called the *symptotic* point. If the temperature be raised beyond this point, pv will no longer give on compression a maximum and a minimum, but only the one point in which both may be supposed to coincide, a thing which is noticed in the case of hydrogen at the ordinary temperature. The author discusses mathematically certain variations in the different properties of gases in the region of the symptotic point.

H. C.

Velocity of Etherification. By V. KISTYAKOFFSKY (*J. Russ. Chem. Soc.*, **22**, 474—476).—The author has deduced the constant of velocity for the etherification of organic acids under the influence of inorganic acids, from experiments made in conformity with the following equations—

$$\frac{dx}{dt} = (a - x)k - xk_1,$$

and

$$0 = (a - \xi)k - \xi k_1,$$

in which a denotes the quantity of organic acid taken, x the quantity of ethereal salt formed, t the time, k and k_1 the constants for the formation and decomposition of the ether: ξ is the value of x for which there is equilibrium between the opposing reactions. Large quantities of water and of alcohol were taken in proportion to the quantity of

organic acid, so that these might be assumed to remain constant during the reaction. On integration, the equations give $k = \frac{\xi}{at} \log \frac{\xi}{\xi - x}$, $k_1 = \frac{a - \xi}{at} \log \frac{\xi}{\xi - x}$, from which $k + k_1 = \frac{1}{t} \log \frac{\xi}{\xi - x}$, the most useful form for calculation.

The quantity of inorganic acid used was less than that of the organic acid present. Under these circumstances it was found that the expression $\frac{1}{t} \log \frac{\xi}{\xi - x}$ was, indeed, appreciably constant. The value of the constant thus obtained diminished as the quantity of water present was increased, and was proportional to the electrical conductivity of the solution when one inorganic acid was substituted for another.

The amount of organic acid converted into ethereal salt when equilibrium had taken place, was found to be proportional to the amount of it originally present in the solution. J. W.

Attempt to found a Chemical Theory on a Basis of Physical Comparison. By G. JAUMANN (*Monatsh.*, **13**, 523—566).—This paper contains an attempt to formulate a theory which might take the place of the atomic theory. It is purely inductive in all its parts, and does not start with preconceived ideas as to the constitution of matter or the nature of the change to be observed, but demands only for the explanation of stoichiometric phenomena the existence of a simple physical principle, such as holds for all other physical changes, and only such definite conceptions as are necessary for the application of this principle. If in physical structure all substances are alike, their chemical behaviour is determined by the numerical value of a single property on which all chemical properties depend, and which may be called the chemical condition or the *chemical*. Differences in the values of this property are, as the author shows, approximately measurable, and determine the changes which will take place in given substances under certain conditions. Application of the principle to a number of different cases is made in the paper. H. C.

Inorganic Chemistry.

The Relative Densities of Hydrogen and Oxygen. By Lord RAYLEIGH (*Proc. Roy. Soc.*, **50**, 448—463; compare Abstr., 1888, 643; 1890, 330).—The author has made further determinations of the relative densities of hydrogen and oxygen. The gases were prepared by the electrolysis of water, passed over heated copper or copper oxide free from sulphur, and dried by passing over potash and phosphoric anhydride; suspended matter was arrested by a tube packed with glass wool. A vacuum globe was then filled with the gas to be experimented on and weighed. Oxygen was thus found to be 15.882

times as heavy as hydrogen at mean temperature and barometric pressure. The result is probably accurate to 0.0003 of the whole.

W. J. P.

Preparing Silicon and Aluminium Chlorides. By H. N. WARREN (*Chem. News*, **66**, 113—114).—Silicon chloride, mixed with but little ferric chloride and readily purified by redistillation, is obtained by passing chlorine into siliconeisen, containing 15 per cent. of silicon, heated to redness in a tubulated clay retort, and retaining the less volatile ferric chloride in the upper part of a suitable adapter, while the lower part is cooled in a freezing mixture to condense the silicon chloride. By using hydrochloric acid gas instead of chlorine, ferrous chloride, and the more volatile siliconchloroform, SiHCl_3 , are obtained.

By the action of chlorine on an alloy of iron with 10 per cent. of aluminium, aluminium chloride is produced, which can be purified by distillation from iron borings. When the pulverised alloy is previously mixed with sodium chloride, the passage of chlorine gives rise to the sublimation of aluminium sodium chloride.

D. A. L.

Dehydration of Silver Oxide. By M. CAREY LEA (*Amer. Jour. Sci.*, **261**, 249—250).—The author has proved by a series of careful experiments that precipitated silver oxide obstinately retains some water when dried for 40 hours at a temperature of 100° . Even a temperature of 130 — 135° fails to expel the last traces of moisture. When heated to 160 — 165° , it becomes anhydrous, but also loses a little oxygen.

The conclusion to be drawn would apparently be that the point at which the last portions of water were driven off was very close to that at which oxygen began to be disengaged; but the author has shown that oxygen is lost long before the last portions of water escape. If silver oxide, after being thoroughly dried at 100° , is moistened with dilute hydrochloric acid, a chloride is obtained of a deep lilac colour, showing the formation of an argentous compound.

L. DE K.

Decomposition of Strontium Bromate by Heat. By A. POTILITZIN (*J. Russ. Chem. Soc.*, **22**, 454—469).—Strontium bromate crystallises in monoclinic prisms with 1 mol. H_2O , which it loses at 120° . The anhydrous salt begins to decompose perceptibly at 240° without melting, the decomposition taking place chiefly in two directions, namely, into strontium bromide and oxygen, and into strontium oxide, bromine, and oxygen. The first reaction is the principal one;

Tempera- ture.	Salt taken, gram.	Time for complete decomposition.	Total loss of weight per cent.	SrO formed per cent.
252°	0.802	8 hrs. 15 m.	33.91	5.57
265	0.540	3 „ 10 „	30.52	2.79
269— 270°	0.749	1 „ 30 „	28.98	—
271°	0.7895	1 „ 54 „	28.46	0.56
271	0.9855	1 „ 40 „	28.31	—
273	0.7275	1 „ 10 „	28.38	0.55
287	0.5698	0 „ 32 „	28.39	0.52

the extent to which it occurs, however, varying considerably with the temperature.

The table, p. 11, contains a summary of the quantitative results arrived at by the author. J. W.

Action of Silver Oxide on Magnesium Nitrate. By A. KORMILITZIN (*J. Russ. Chem. Soc.*, **22**, 488—492).—Solutions of freshly crystallised magnesium nitrate, $\text{Mg}(\text{NO}_3)_2 + 6\text{H}_2\text{O}$, were shaken up in the dark with weighed quantities of freshly precipitated silver oxide. After a given time, the solution was filtered off, and both it and the residue analysed, in order to determine the proportion of silver oxide which had been converted into silver nitrate. The following table contains a summary of the author's results :—

Duration of experiment.	Percentage change with		
	$\frac{1}{3}$ -Normal $\text{Mg}(\text{NO}_3)_2$.	Normal $\text{Mg}(\text{NO}_3)_2$.	3-Normal $\text{Mg}(\text{NO}_3)_2$.
1 day	0·15	0·41	0·51
2 days.....	0·17	0·47	0·54
14 „	0·24	0·68	0·75

The amount of change is thus not proportional to the concentration of the magnesium nitrate solution, although it is so, approximately, when we pass from the $\frac{1}{3}$ -normal to the normal solution.

J. W.

Atomic Weight of Copper. By T. W. RICHARDS (*Chem. News*, **65**, 236—237, 244—245, 260—261, 265—268, 281—282, 293, 302—303; **66**, 7—9, 20—21, 29—31, 47—48, 57—58, 74, 82—83; compare *Abstr.*, 1891, 805).—The atomic weight of copper is deduced from : I. The analysis of cupric sulphate. II. The synthesis of cupric sulphate. III. The analysis of cupric oxide. All calculations are based on the atomic weights: oxygen, 16·000; barium, 137·10; bromine, 79·955; carbon, 12·002; hydrogen, 1·008; silver, 107·930; sodium, 23·053; sulphur, 32·060.

The standard weights used (described in *Proc. Amer. Acad. Arts Sci.*, **25**, 196) were carefully compared with the standards of the Washington Bureau of Weights and Measures. Excepting in the first series of experiments on cupric sulphate, the method of weighing by substitution was used. All weighings were reduced to the vacuum standard.

Full details are given of the methods used in the purification of the materials and reagents employed.

I. Analysis of Cupric Sulphate.—For the first series of analyses the cupric sulphate was coarsely powdered, dried to constant weight over a mixture of crystallised and partially dehydrated cupric sulphate, and the copper determined by electrolysis. The sulphuric acid set free was determined by sodium carbonate and by weighing

the sodium sulphate formed. In the third place, the loss of water at 250° was also determined. The sum of the constituents was 99·87, the water lost at 250° being 35·958 per cent., whereas, if $\text{Cu} = 63\cdot60$ or $63\cdot33$, the total water present should be $36\cdot0695$ or $36\cdot109$ respectively.

In the second series of analyses, the cupric sulphate was dried at 255° in a platinum crucible, and then treated with 20 drops of pure sulphuric acid, and the whole kept at 365° for $3\frac{1}{2}$ hours. There was a further loss of moisture, amounting to 0·108 per cent. of the crystallised sulphate. The dry sulphate was dissolved, and the clear solution electrolysed in a platinum crucible, previously coated inside with copper. After 120 hours, the weak current was interrupted, and the acid rapidly washed into a platinum bottle. Rather less than the required amount of sodium carbonate was weighed out, ignited at a dull-red heat to constant weight, dissolved in water, and added to the acid in the bottle. The very slight excess of acid was titrated with sodium hydroxide, using methyl-orange as indicator. The neutral solution was evaporated, and the residue of sodium sulphate fused and weighed. From the results the following ratios were deduced:—

$\text{Na}_2\text{CO}_3 : \text{Cu} = 106\cdot108 : 63\cdot606$, and $\text{Na}_2\text{SO}_4 : \text{Cu} = 142\cdot166 : 63\cdot595$.

Including the water driven off between 255° and 365° , the sum of the constituents determined reached 99·954.

The third series of analyses was carried out by the same method but with greater refinement. To ascertain whether the method of drying affected the percentage of acid present, the first sample was not dried, the second was only heated at 250° , the third was heated at 365° , after addition of sulphuric acid. The SO_4 found was 38·443, 38·435, and 38·431 per cent. in the three cases.

The fourth experiment of the series was not of the same order of accuracy. The SO_4 was weighed as BaSO_4 . The adhering barium chloride being estimated and allowed for, this experiment gave $\text{SO}_4 = 38\cdot434$ per cent.

This series gave, as the sum of the constituents determined, 99·951. The deficiency was proved to be due to water still retained at 360° . It was determined by heating to dull redness, and estimating the sulphuric anhydride driven off at the same time. The difference between the loss and the sulphuric anhydride driven off amounted to 0·042 per cent. as a mean of four experiments, varying from 0·019 to 0·055. The final result of these analyses gave:—

Water lost at $360\text{--}400^{\circ}$	36·067 per cent.
Water lost between 400° and redness....	0·042 ,,
Copper.....	25·449 ,,
SO_4	38·436 ,,
	<hr/>
	99·994 ,,

There is an unavoidable excess of water, due to mother liquor enclosed during crystallisation.

Rejecting the ratios including the water of crystallisation, the atomic weight of copper may be calculated as follows:—

Ratio.	Lowest.	Highest.	Experimental mean.
1. $(\text{CuSO}_4 - \text{Cu}) : \text{Cu} \dots$	(63·53)	63·62	63·593
2. $\text{Na}_2\text{CO}_3 : \text{Cu} \dots\dots\dots$	63·592	63·604	63·600
3. $\text{Na}_2\text{SO}_4 : \text{Cu} \dots\dots\dots$	63·59	63·61	63·607
4. $\text{Na}_2\text{CO}_3 : \text{CuSO}_4 \dots\dots$	63·61	63·64	63·621
5. $\text{Na}_2\text{SO}_4 : \text{CuSO}_4 \dots\dots$	63·59	63·67	63·641
6. $\text{BaSO}_4 : \text{Cu} \dots\dots\dots$	(63·57)	(63·63)	63·603
7. $\text{BaSO}_4 : \text{CuSO}_4 \dots\dots$	(63·54)	(63·69)	63·625
Average			63·612
Average omitting 5 and 7 ..			63·605

The foregoing experiments furnish data for the calculation of the atomic weight of sulphur. As the average of eight experiments, $S = 32\cdot063$; omitting three experiments of less value than the remainder, $S = 32\cdot075$.

II. The Synthesis of Cupric Sulphate.—Cupric sulphate was synthesised from metallic copper and from cupric oxide. Pure electrolytic copper was dissolved by the purest nitric acid in a platinum bottle supplied with bulb tubes to act as a spray condenser. The solution was evaporated with a slight excess of pure sulphuric acid in a platinum dish. The residue was gradually heated to 400° , and cooled in a phosphoric anhydride vacuum desiccator. It was always found to contain free sulphuric acid, and hence no trustworthy results were obtained. The cupric oxide (for preparation see *Proc. Amer. Acad. Arts Sci.*, 25, 199) was treated in the same manner as the copper. The average percentage of cupric oxide in the sulphate formed was 49·838 (three experiments), as compared with 49·856 if $\text{Cu} = 63\cdot6$. The close agreement is due solely to the effect of opposing errors.

III. The Analysis of Cupric Oxide.—The cupric oxide, when tested by reduction with carbon monoxide, was found to retain no appreciable amount of water at a red heat. It did not contain any carbonic anhydride or any higher oxides or nitrogen oxides. A large number of experiments, in which the cupric oxide, after varied treatment, was entirely dissolved, proved: (1.) That cupric oxide, prepared by ignition of the oxynitrate after Hampe's method, contained between four and five times its volume of occluded gas. (2.) Ignition of this oxide at bright redness expelled a portion of the gas. The temperature of the ignition was apparently higher than that used by Hampe. (3.) Beyond a certain limit, the time of ignition made no important difference. (4.) The gas was not absorbed during cooling. (5.) Specimens of cupric oxide, prepared in different ways, contained very different amounts of gas.

A series of three more carefully carried out experiments on pure cupric oxide, similar to that used in the synthesis of cupric sulphate, gave the percentages of occluded gases as 0·088 nitrogen and 0·004

oxygen. This, applied as a correction to the two best results obtained in the analysis of cupric oxide, gave $\text{Cu} = 63.605$.

The indirect results from the synthesis of cupric sulphate from the oxide, corrected in the same way, gave 63.603.

It is concluded that Hampe's work was subject to serious error, for which it is now impossible to make correction.

A summary of the results obtained by the author between 1887 and 1891 gives, for the atomic weight of copper, general average: (a) of 11 series, 63.610; (b) of 43 determinations, 63.606. Average of the five most trustworthy series, 63.604. W. T.

Ternary Alloys. Part V. Determination of Various Critical Curves, their Tie Lines and Limiting Points. By C. R. A. WRIGHT (*Proc. Roy. Soc.*, 50, 372—395; compare Abstr., 1891, 1158).—The author has continued the experiments with mixtures of chloroform, water, and acetic acid, and finds the average composition for the "limiting point" at 18° to be 42.16 per cent. of chloroform, 16.21 of water, and 41.63 of acetic acid. It is noteworthy that the chloroform and water are here present almost in the molecular ratio $2\text{CHCl}_3, 5\text{H}_2\text{O}$; this may, however, be merely a coincidence.

The percentages of lead, tin, and zinc contained in a mixture of these metals at 565—570°, at the limiting point, are approximately 22, 35, and 43 respectively, whilst at 750—850° the numbers are 24, 32, and 44. Tables are given showing the composition of the alloys of the metals obtained near 650°; the composition corresponding with the limiting point, as deduced from these, is 22.5, 42.5, and 35.0 per cent. of lead, zinc, and tin, respectively. The tie lines on the critical curve show two maxima, one corresponding with the molecular compound Pb_3Sn , the other to SnZn_4 . The ratio between lead and zinc at the limiting point approximates to PbZn_6 at both 650° and 800°.

The limiting point for an alloy of bismuth, zinc, and tin, at 650°, corresponds with percentages of 18.5, 60.0, and 21.5 of these metals respectively.

For alloys of lead, zinc, and silver at about 800°, the limiting point corresponds to 48.2, 6.3, and 45.5 per cent. of the respective constituents. Lead and zinc are present in the proportion of Pb_2Zn , not PbZn_6 , as when tin is the solvent. The effect of the formation of the compounds AgZn_5 and Ag_4Zn_5 on the critical curve is very marked.

The critical composition at about 750° for alloys of bismuth, zinc, and silver is 33.12, 22.25, and 44.63 per cent. respectively, representing a ratio between bismuth and zinc, approximately indicated by BiZn_2 ; when tin is the solvent metal, the corresponding ratio is nearly represented by BiZn_{10} . The formation of the compounds AgZn_5 and Ag_4Zn_5 is indicated on this critical curve, just as on that of the lead-zinc-silver alloys. W. J. P.

Certain Points in the Interaction of Potassium Permanganate and Sulphuric Acid. By F. A. GOOCH and E. W. DANNER (*Amer. J. Sci.* [3], 44, 301—310).—Jones (*Trans.*, 1878, 95), and more recently Brauner, have observed the evolution of oxygen from solu-

tions of potassium permanganate and sulphuric acid during oxidation effected by their means. The authors also find this to be the case, and that the decomposition of the permanganate by the acid increases with the amount of acid present, the time of action, and increase of temperature. A 20 per cent. solution of the acid produces no appreciable effect at ordinary temperatures, and under exposures of a few hours only. In five days, however, a very considerable action takes place at the ordinary temperature, and heating the mixture of acid and permanganate to 80° for an hour and a half is closely comparable in its effect with that brought about by the five days' action at the ordinary temperature.

It appears, from further experiments, that the change is brought about by a tendency towards reduction on the part of the acid. When the acid is not present in proportion greater than 50 per cent. of the mixture, in the early stages of the action the oxygen lost by the permanganate is liberated, but later on the decomposition of the permanganate results in the precipitation of manganese in the form of a higher oxide, or in the retention of the manganese in solution in the form of a higher sulphate.

H. C.

The Passive State of Iron and Steel. Part III. By T. ANDREWS (*Proc. Roy. Soc.*, **49**, 481—488; compare Abstr., 1891, 250).—Considerable differences are to be observed between the relative passivities of wrought iron and hard and soft cast steels, Bessemer steels and Siemens steels; variations in the chemical composition and physical structure of the metals greatly influence the passive state. Wrought iron was found to be less passive than the steels employed, being electropositive to them when placed in nitric acid; the difference of potential established between the two metals was in some cases as much as 0.1 volt. In some instances the wrought iron did not become electropositive until immersed for 2 to 3 hours in the acid; the difference in potential then gradually increased, showing that the wrought iron was slowly becoming less positive than the steel. Wrought iron is electronegative to tungsten steel, and is hence more passive than the metal. The E.M.F. developed in circuit between wrought iron and soft steels containing but little combined carbon, when immersed in cold nitric acid (sp. gr. 1.42), is much less than that developed with hard steels containing more combined carbon. Steels containing a high percentage of combined carbon are more passive than those containing a smaller quantity.

W. J. P.

Action of Nitric Acid on Potassium Dichromate. By G. C. SCHMIDT (*Ber.*, **25**, 2917—2918).—In 1871, Darmstädter described the formation of two crystalline compounds, $\text{Cr}_2\text{O}_5(\text{OK})\text{NO}_2$ and $\text{Cr}_3\text{O}_8(\text{OK})\text{NO}_2$, by the action of nitric acid on potassium dichromate (this Journ., 1871, 199). The author, repeating Darmstädter's experiments, obtained potassium tetrachromate, $\text{K}_2\text{Cr}_4\text{O}_{13}$, but was unable in any way to obtain a compound containing nitrogen. The substances Darmstädter obtained were undoubtedly mixtures of the tetrachromate with potassium nitrate.

L. T. T.

Ammonium Chromates. By E. MAUMENÉ (*Bull. Soc. Chim.* [3], 7, 174—179).—Concentrated aqueous chromic acid or potassium dichromate, when neutralised by ammonia, deposits ammonium chromate, $(\text{NH}_4)_2\text{CrO}_4$, in yellow, crystalline tufts, which resemble those of the potassium salt, but soon lose ammonia, and change into the dichromate. The salt is best crystallised by evaporating the slightly ammoniacal solution over quicklime, and should be kept in sealed vessels.

Ammonium chromate yields a brown oxide, CrO_2 , when heated at 204° , identical with the oxide which was described by Vauquelin as precipitated on heating the aqueous solution, although in all probability it is formed only on the superheated sides of the vessel. When the temperature is raised to 220 — 225° , explosive decomposition occurs, and the oxide CrO is formed, which, however, takes fire at once, and burns to the green oxide Cr_2O_3 ; it is probable that the compound $\text{N}_2\text{H}_4\text{CrO}_3$ is formed as an intermediate product. The brown oxide is soluble in aqueous chromic acid or alkaline dichromates, forming brown solutions, from which it is reprecipitated by excess of water.

The deliquescent, crystalline, double chromate of ammonium and potassium, $(\text{NH}_4)_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$, prepared by dissolving potassium dichromate in concentrated aqueous ammonia, and evaporating the yellow, syrupy solution over quicklime, turns brown at 240° , owing probably to the formation of the chromate of a base $\text{N}_2\text{H}_6\text{O}$, and is completely decomposed at 270° , the green oxide Cr_2O_3 remaining.

JN. W.

Preparation of Vanadyl Trichloride: Extraction of Vanadium from its Ores. By L. L'HÔTE (*Ann. Chim. Phys.* [6], 22, 407—412).—For the extraction of vanadium from its ores the author takes advantage of the volatility of vanadyl trichloride. The finely divided mineral is intimately mixed with about one-quarter of its weight of lamp-black and a little oil, and ignited to volatilise the arsenic and zinc; the calcined product is then slowly heated to 300° in a stream of dry chlorine, and the vanadyl trichloride collected in tubes immersed in a freezing mixture.

When it is desired to determine the quantity of vanadium in an ore, the above method is employed, and the vanadyl trichloride is collected in a series of bulbs containing distilled water; the vanadic acid is then reduced with zinc, and estimated volumetrically with the aid of potassium permanganate.

Samples of bauxite, examined in this way, were found to contain 0.03 to 0.05 gram of vanadium per kilo.; two samples of pitchblende from Bohemia contained 1.62 and 1.40 grams of vanadium per kilo. respectively.

F. S. K.

Refining Gold, Silver, and Platinum. By H. N. WARREN (*Chem. News*, 66, 140—141).—Gold is separated from its alloys by melting them with $2\frac{1}{2}$ times their weight of silver, then parting with nitric acid; the silver being subsequently precipitated by copper and the latter metal by iron. By treating silver platinum alloys with nitric acid, all the former and all or part of the latter metal are dissolved; but by precipitating both metals from this solution by copper,

and again treating the precipitate with nitric acid, the silver only is dissolved.

D. A. L.

Mineralogical Chemistry.

Beyrichite from Altenkirchen. By H. LASPEYRES (*Zeit. Kryst. Min.*, 20, 535—550).—An examination of this very rare mineral from the Lammerichskaule mine, at Altenkirchen, in the Siegen district, has, in the main, confirmed the results published by Liebe in 1871. Beyrichite bears the same relationship to millerite that augite does to uralite. Beyrichite is the mother mineral from which millerite has been formed by a rearrangement of the molecules. Both minerals have the same crystalline form and composition, but different physical properties. Analysis of beyrichite gave results in accord with the formula $(\text{NiCoFe})\text{S}$.

B. H. B.

Cobaltiferous and Nickeliferous Iron Pyrites from Müsen. By H. LASPEYRES (*Zeit. Kryst. Min.*, 20, 553—555).—The crystals examined by the author occurred in a fissure in brown spar at the Heinrichs-segen mine, at Müsen. Analysis gave the following results:—

S.	Fe.	Co.	Ni.	Total.
51.35	42.68	1.97	4.13	100.13

The mineral appears to consist of a crystal of iron pyrites covered by a parallel deposition of polydymite crystals on its surface.

B. H. B.

Pseudobrookite, Hämatite, and Anhydrite as Sublimation Products. By B. Doss (*Zeit. Kryst. Min.*, 20, 566—587).—The author describes the occurrence of pseudobrookite, hæmatite, and anhydrite as sublimation products in the furnaces of the Hermania soda works at Schönebeck. Numerous other minerals of recent formation have previously been found at the same works, the list including: (1) specular iron ore, (2) magnetite, (3) iron pyrites, (4) magnetic pyrites, (5) a tetragonal calcium aluminium silicate isomorphous with gehlenite, (6) a calcium silicate, (7) crystallised lime, (8) glauberite, (9) gaylussite, (10) rhombic silico-carbonate, and (11) octahedral crystals of sodium fluorophosphate ($\text{NaF}, 2\text{Na}_3\text{PO}_4 + 18\text{H}_2\text{O}$), with 1.2 to 1.3 per cent. of vanadic acid. Pseudobrookite has not hitherto been found as a sublimation product in technical working. The analysis of the Schönebeck product gave results in accord with the formula Fe_2TiO_5 .

B. H. B.

Soda from the Alkaline Waters of Owen's Lake. By E. LE NEVE FOSTER (*Zeit. Kryst. Min.*, 20, 631; from *Proc. Colorado Sci. Soc.*, 3, 245—254).—The author describes the manner in which soda is obtained from the highly alkaline water of Owen's Lake in Myo Co., California. The lake, which is at an altitude of some 3,600 feet, lies in a basin apparently of volcanic origin between the Sierra Nevada

and the Myo chain of mountains. The lake has no outlet and its chief feeder is the Owen's River, coming in from the north. The composition of the water is as follows:—

SiO ₂ .	MgCO ₃ .	KCl.	NaCl.	Na ₂ SO ₄ .	Na ₄ B ₂ O ₇ .	Na ₂ CO ₃ .
0·220	0·055	3·137	29·415	11·080	0·475	26·963
	HNaCO ₃ .		Al ₂ O ₃ , Fe ₂ O ₃ .		Total.	
	5·715		0·038		77·098	

The water of Lake Albert contains 39·172, Mono Lake 53·473, and Lake Bagtown 129·01 of solids per litre. The water is pumped into reservoirs, and the soda obtained by evaporation. In 1889, in this way 1,000 tons of soda was obtained, and in 1890 double that amount.

B. H. B.

Synthesis of Minerals of the Hauyn Group. By J. MOROZIEWICZ (*Jahrb. f. Min.*, 1892, ii, Mem. 139—141).—It has been shown by Lemberg that hauyn and sodalite, at an intense heat, lose sulphuric acid and chlorine respectively. For this reason, it has been found impossible to prepare these minerals artificially in a crystalline state. The results of the author's experiments on the synthesis of hauyn are as follows:—1. A mixture of 65 parts of SiO₂, 3H₂O with 44 parts of Al₂O₃, 3H₂O and 33 parts of gypsum was heated for 6 hours in an excess of Glauber's salt in a platinum crucible. The melted mass was treated with cold distilled water, filtered, and washed until the filtrate gave no precipitate with barium hydroxide. The resulting product, an infusible, greyish powder, was found under the microscope to contain crystals of hauyn. 2. The same mixture treated with molten sodium sulphate and sodium chloride gave some very fine and regular crystals, together with columnar twin crystals of sodalite. 3. The same mixture inserted in sodium chloride alone gave crystals apparently consisting of pure sodalite. The author is continuing his experiments with a view of attaining further information regarding the processes obtaining in the formation of hauyn and sodalite in lava.

B. H. B.

The Chlorite Group. By G. TSCHERMAK and E. LUDWIG (*Jahrb. f. Min.*, 1892, ii, Ref. 227—232; from *Min. petr. Mitth.*, 12, 32—39).—Numerous analyses are given in support of Tschermak's theory that the chemical structure of the chlorites may be explained by dividing this group of minerals into two sub-groups, orthochlorites and leptochlorites. The orthochlorites are believed to be mixtures of two end products, serpentine and amesite; whilst, for the leptochlorites four other fundamental compounds are assumed, strigovite, chloritoïd, and two derivatives of amesite. Representing these minerals by symbols, the chlorites may be classed as follows:—

A. *Orthochlorites*.—Pennine, Sp₃At₂; clinochlore, SpAt; prochlorite, Sp₃At₂ to Sp₃At₇; corundophilite, Sp₃At₂ to SpAt₄; amesite, SpAt₄ to At.

B. *Leptochlorites*.—I. Daphnite, (At'At)₂Sp₄; chamoisite, (At'At)₃Sp₄. II. Metachlorite, (StAt₃)₂Sp₃; clementite, (StAt₂)₂Sp; cronstedtite StAt; euralite, St₄At₃ (strigovite = St). III. Diabantite, Ct₄Sp₇

aphrosiderite, $(\text{CtAt})_6\text{Sp}_4$; delessite, $(\text{CtAt})_2\text{Sp}_5$ to CtSp ; rumfite, $(\text{CtAt}')_4\text{Sp}$ (chloritoid = Ct).

C. *Mixed Alteration Products*.—Tabergite, pyrosklerite, loganite, pseudophite, vermiculite, hallite, berlanite, enophite.

D. *Chlorites not yet Defined*.—Epichlorite, grengesite, melanolith.

B. H. B.

Meteoric Iron. By E. COHEN and E. WEINSCHENK (*Jahrb. f. Min.*, 1892, ii, Ref. 244—246; from *Annalen des k.k. Naturhistorischen Hof-museums*, 6, 131—165).—The authors have endeavoured to solve a number of problems connected with meteoric iron.

1. Cohenite seems to be confined to the Arva group. The composition of cohenite from the Magura meteoric iron is in accord with the formula $(\text{FeNiCo})_3\text{C}$, whilst that of the iron carbide from the Wichita meteoric iron is in accord with the formula $(\text{FeNiCo})_4\text{C}$.

2. The composition of schreibersite is in many cases constant in that the ratio of $\text{Fe} + \text{Ni} + \text{Co}$ to P is fixed; its formula being $(\text{FeNiCo})_3\text{P}$. The new analyses of schreibersite from the Toluca, Glorieta Mountain, and Hraschina meteorites confirm this view.

3. The theory propounded by E. Cohen that the hexahedral iron (kamazite) has a constant composition (about 7 per cent. $\text{Ni} + \text{Co}$) is supported by the analysis of the meteoric iron from the Hex River Mountains, Cape Colony. The mean composition of kamazite corresponds with the formula Fe_{14}Ni .

4. Two varieties of tænite occur in meteoric iron. One is tin-white, flexible, rich in $\text{Ni} + \text{Co}$, and contains no appreciable quantity of carbon. To this class belongs the tænite from the Toluca, the Wichita, and the Glorieta Mountain meteorites. The second variety presents a more greyish colour, less lustre, less flexibility, and less nickel and cobalt, whilst carbon is present in appreciable quantities. To this class belongs the tænite from the Staunton and Magura meteorites.

B. H. B.

Physiological Chemistry.

Absorption of Oxygen and Formation of Carbonic Anhydride in Human Respiration. By W. MARCET (*Proc. Roy. Soc.*, 50, 58—75; compare *Abstr.*, 1891, 1270).—From experiments made on two healthy persons, one 63 and the other 21 years of age, the author arrives at the following conclusions:—(1.) The percentage of carbonic anhydride, oxygen, or nitrogen in the air expired alters with the person experimented on, but the proportion of each gas varies but slightly up to a period of about $4\frac{1}{2}$ hours after the midday meal. (2.) The mean ratio between the oxygen consumed and the carbonic anhydride exhaled is 0.871. (3.) The mean volume of oxygen absorbed per minute is 34.3 c.c. (4.) The mean volume of oxygen absorbed is 0.75 per cent. of the air inspired, and was nearly the same with both subjects. 3.63 per cent. of the oxygen inhaled was absorbed. (5.) The mean weight of oxygen consumed per hour by the older man was 0.355 gram per kilo. of body weight; the weight

absorbed by the younger man was 0.380 gram. (6.) The weight of carbonic anhydride expired was notably greater in the younger than in the older man, and corresponded approximately with the greater consumption of oxygen by the former.

The following results were obtained from an investigation into the respiration of air containing 2.5—4 per cent. of carbonic anhydride:— (1.) The proportion of oxygen in the air expired is slightly greater than in ordinary breathing. (2.) The mean ratio of oxygen absorbed and the carbonic anhydride expired is small, being 0.654 and 0.567 for the older and younger man respectively, as against a mean of 0.871 in ordinary breathing. (3.) The volume of oxygen absorbed is 3—4 times as great as in ordinary breathing. (4.) The proportion of oxygen absorbed from the air inspired is about twice as great as when pure air is breathed. (5.) The weight of oxygen consumed by the body undergoes an increase of about 20 per cent. (6.) The total weight of carbonic anhydride expired is reduced by about 12 per cent. When such air is breathed, therefore, a considerable amount of oxygen must remain in the blood to be transformed into an excess of carbonic anhydride in addition to the proportion required for the other functions of the body.

W. J. P.

Action of Fatiguing Muscular Work on the Respiratory Interchange. By A. LOEWY (*Pflüger's Archiv*, 49, 405—422).—During ordinary muscular activity the combustion processes in the body take the same direction as during rest; this is shown by the respiratory quotient remaining constant. When the work becomes excessive, this normal is upset and the respiratory quotient rises. The muscular katabolism is not directly dependent on the work actually performed, but on the amount of muscular energy expended; this is a variable quantity, as under favourable conditions muscle works more economically (that is, with a less loss of heat) than when the conditions are unfavourable; one of the unfavourable conditions is fatigue. In other words, during fatigue more muscular activity is expended in doing a given amount of work, than when the muscle is fresh. At the end of a period of work the respiratory processes remain increased for a few minutes; if, however, fatigue has supervened, or the work has been done under unfavourable conditions (for instance, with an insufficient supply of oxygen), the respiratory exchanges remain disturbed for a longer period.

W. D. H.

Influence of Acetic Acid on Gaseous Metabolism. By A. MALLÈVRE (*Pflüger's Archiv*, 49, 460—477).—When cellulose is ingested, it undergoes certain putrefactive changes leading to the formation of carbonic anhydride, methane, acetic, and butyric acids. In estimating the nutritive value of cellulose, it is therefore important that we should know the effect which these fatty acids have on metabolism. The present experiments were made on rabbits, and chiefly with acetic acid, which was intravenously injected as sodium acetate. It was found that the quantity of oxygen used by the animal was increased during and after the injection and that the carbonic an-

hydride produced fell relatively; the respiratory quotient was consequently lower; in four experiments the R.Q. was as follows:—

	1.	2.	3.	4.
Before injection.....	1.04	0.77	0.77	0.87
During injection	0.86	0.71	0.69	0.80
After injection	0.76	0.77	0.77	0.79

Other changes noted were increased alkalinity of urine and of the blood, due, doubtless, to the conversion of acetate into carbonate.

The sinking of the respiratory quotient shows that some acetic acid was burnt up; the theoretical R.Q. of acetic acid is 0.5. The R.Q. found never sank so low as this, showing that other materials in the body were being simultaneously oxidised. It is, however, considered that any sparing action exercised by the acetic acid formed from cellulose would be more than counterbalanced by the increased work thrown on the digestive organs, and a consequent larger necessary supply of oxygen.

Nutritive Value of Cellulose. By N. ZUNTZ (*Pflüger's Archiv*, 49, 477—483).—This paper consists of remarks of a general nature on the foregoing, and a critical review of those researches which have attempted to show that cellulose has any great nutritive value.

W. D. H.

Researches on Blood. By L. LILIENFELD (*Chem. Centr.*, 1892, ii, 82—83; from *Arch. Physiol.*, 1892, 115—154).—The small plates which, besides the red and white corpuscles, exist in the blood have been examined by treating them with an artificial digestive fluid; they were found to consist of a granular portion, nucleïn, and a homogeneous portion, chiefly albumin. The nucleïn is separated out by the pepsin ferment from its compound with albumin which exists in the plates, and can then be identified by its chemical reactions.

C. F. B.

Some Results of Transfusion. By H. C. GEELMUYDEN (*Arch. Anat. und Physiol., physiol. Abth.*, 1892, 480—496).—If a large quantity of living blood is introduced into the vascular system of a dog, the animal remains healthy. Its excretion of nitrogen is, however, increased for several days. The increase is not from excess of proteid food, and the body weight does not fall. The increase of nitrogen can be accounted for by the excess of nitrogenous matter introduced into the blood. The increase lasts as long as the increase in the blood constituents does; when this reaches a maximum, the new blood is katabolised and the animal, as regards both blood and nitrogenous output, returns to the normal. Extravasation of blood is never found. The opinion is expressed that the seat of the destruction of the corpuscles is the blood stream itself. There is, however, no solution of the hæmoglobin from the corpuscles; not once was the serum found to be red.

W. D. H.

Pancreatic Juice in Different Animals. By V. D. HARRIS and W. J. GOW (*J. Physiol.*, 13, 469—492).—From the examination of the

ferments of the pancreas in a large number of animals, the tryptic ferment was far the most constantly present and the more resistant; then the rennetic, and then the diastatic. The fat splitting ferment is often absent, and it is always readily destroyed, for instance, by preserving the pancreas in alcohol. No special fat-emulsifying agent was ever found. Of the animals examined, four only (man, pig, ox, sea-eagle) were in the first class as regards the activities of all their pancreatic ferments.

A few experiments with pancreases removed from individuals who had died of wasting disease showed that the activity of the ferments was much diminished.

In pig's pancreas, no inversive ferment was found. Fresh pig's pancreas, however, converts raw starch into dextrin, but not into dextrose. The diastatic action on cooked starch was not hindered by the presence of phenol (1 in 130) or of mercuric chloride (1 in 1000).

W. D. H.

Conversion of Maltose into Dextrose. By L. E. SHORE and M. C. TEBB (*Proc. Physiol. Soc.*, 1892, 19—20).—Various organs (intestinal wall, pancreas, lymphoid structures) were dried at a low temperature and added to solutions of maltose. The largest change was obtained with the intestinal mucous membrane from the pig. After 21 hours' action in the warm bath, the sugars present were 19 per cent. maltose, and 81 per cent. dextrose. In another experiment (the mucous membrane being freed from Peyer's patches), the numbers were 35·3 and 64·7 respectively. The Peyer's patches gave 63·3 and 36·7. Brown and Heron found, on the contrary, that lymphoid tissue was more active than ordinary mucous membrane. In the present research, lymphatic gland gave 72 and 28. With pancreas, the action was still less, 76 and 24. Pancreatic extracts gave only a trace of dextrose after 24 hours.

The experiments show that the change of maltose into dextrose is not accomplished by the pancreas but by the intestine, and, further, not so much by the lymphoid tissue as by the mucous membrane of the gut; but whether it is effected by the secretion poured out into the intestinal cavity, or by the cells through which the solutions pass during absorption, is not indicated by these experiments.

W. D. H.

Fluorine Compounds in the Organism. By J. BRANDL and H. TAPPEINER (*Zeit. Biol.*, 27, 518—539).—Experiments on dogs which were fed on food admixed with sodium fluoride show that the soluble fluorine compound administered causes an increase in the amount of that element in the body. A great part is deposited in the bones in the form of a crystalline compound, which probably is identical with fluor-spar.

W. D. H.

Absorption of Iron. By A. J. KUNKEL (*Pflüger's Archiv*, 50, 1—24).—The present experiments on animals show that small quantities of iron are absorbed when that metal is administered in the form of inorganic salts. It appears to collect in the liver. It is possible that these substances may be changed in the intestine into something like Bunge's hæmatogen before absorption. These hæma-

togenous substances appear to be ill-defined at present as chemical units, and it is probable that the organic iron compounds in various foods are not all identical.

W. D. H.

Demonstration of the Presence of Iron in Chromatin by Microchemical Methods. By A. B. MACALLUM (*Proc. Roy. Soc.*, 50, 277—286).—The presence of iron in the chromatin of cellular elements of such tissues as are almost free from hæmatin may be proved by running a drop of freshly prepared ammonium sulphide on to the fresh section; a cover glass is then placed on the latter and the edges sealed with glycerol. On maintaining the preparation at a temperature of 60° for some days, the chromatin nodules become stained light green to black, thus proving the presence of iron. Albuminate iron or inorganic iron compounds may be previously removed, if necessary, by treatment with Bunge's fluid.

Iron was found in the chromatin of the cells of numerous organs and tissues of *Necturus*, *Oniscus*, and various placentæ. It is also present in the chromatin of the pollen cells of *Dianthus*, *Cucurbita*, *Narcissus*, and *Hyacinthus*, and in the gonidia of *Cystopus candidus*.

W. J. P.

Absorption of Fats. By O. FRANK (*Arch. Anat. und Physiol., physiol. Abth.*, 1892, 497—512).—In some experiments on dogs, analysis of the intestinal contents shows that, when the thoracic duct is ligatured, a very large absorption of the fatty acids from the fat in the food goes on. A few analyses of the blood were performed, but these appear to be insufficient for purposes of comparison. Most, however, show a rise in the percentage of fat and lecithin as compared with the normal. Soaps and cholesterol are apparently unaltered in quantity.

W. D. H.

Nutritive Value of Alcohol. By F. STRASSMANN (*Pflüger's Archiv*, 49, 315—330).—The statement of Bödlander (*ibid.*, 32) that 95 per cent. of the alcohol taken under ordinary conditions is used by the organism should be amended; the correct number is 90 per cent. Without entering into the question of the therapeutic value of alcohol, it is thus seen that it is a nutritive agent. There are, however, many other substances with the same or even greater nutritive value, without the poisonous action of alcohol.

W. D. H.

Digestibility and Nutritive Value of Bread. By N. ZUNTZ and A. MAGNUS-LEVY (*Pflüger's Archiv*, 49, 438—460).—In men not doing excessive mechanical work, more than half of the oxygen used up is consumed in muscular activity.

A diet very poor in proteid is well assimilated by the human digestive tract; and addition of starch to bread does not impair its nutritive value. One must not, however, go too far in the restriction of proteid. No injurious influence was observed by the addition of 60 grams of alcohol.

During feeding on white bread and butter, the digestive work requires at least 10 per cent. more oxygen than when the digestive

organs are at rest; and more than 5 per cent. of the nutriment given is consumed in the assimilation of food.

W. D. H.

Formation of Sugar in the Liver. By J. SEEGEN (*Chem. Centr.*, 1892, ii, 84; from *Arch. Physiol.*, 1892, 34—53).—A reply to Pflüger (*Chem. Centr.*, 1891, ii, 713, and 1892, i, 37), upholding the author's view that sugar is produced by the normal action of the liver. He thinks that the proteids contained in nitrogenous food are completely decomposed in this organ, the nitrogen being converted into carbamide, and the carbon into sugar, the latter, in his opinion, being the source of all the energy of the animal body.

C. F. B.

Deposition of Albumin during the Fattening of Full Grown Animals. By T. PFEIFFER and G. KALB (*Bied. Centr.*, 21, 579—588; from *Landw. Jahrb.*, 1892, 175—203).—The object of the experiments was to ascertain whether there is a continuous deposition of albumin during a long period of fattening (about 100 days). There were two experiments, each with two full grown, lean sheep (weighing about 42 and 35 kilos.). In the one experiment, the sheep (Nos. 1 and 2) had each day:—hay (500 grams), salt (10 grams), crushed beans (400 grams), and earth-nut cake (200 grams); in the other experiment (sheep 3 and 4) the same amounts of hay and salt were given with crushed beans (200 grams) and crushed barley (320 grams). The amount of water consumed was determined daily. The amount and composition of the excrement, and from this the amounts of food constituents digested, were determined at the beginning, in the middle, and at the end of the experiment. The results are given in tables. It is shown that, as the fattening progresses, there is generally no very considerable difference observed in the digestibility of the food, but the following table shows that the digestion coefficients did fall somewhat:—

	Sheep No. 1.	Sheep No. 2.	Sheep No. 3.	Sheep No. 4.
1st period	76·14	75·53	75·06	72·14
2nd period	71·75	74·17	72·81	72·76
3rd period	74·46	74·45	72·21	69·42

The albumin of the food in Experiment 1 was more completely digested than that of Experiment 2. In the digestibility of the ether extracts there were great differences, owing, the author thinks, to the presence of soluble substances in the fæces produced by fermentation in the intestines. To overcome this difficulty, separate determinations of fat, free fatty acids, and other substances soluble in ether should be made; but experiments hitherto made in this direction gave only negative results.

The decomposition of albumin remained fairly constant in the three periods of Experiment 1, but in Experiment 2, there was an unmistakable rise in the second and third periods as compared with the first. The results are, however, somewhat affected by the consumption of water being insufficient in the case of sheep 1, 2, and 3. It is pointed out that an insufficiency of water may give rise to totally

reversed results, so that, in experiments with animals, there should be no restraint as regards amount of water.

A table is given, showing the nitrogen balance in grams per day. When the amount of nitrogen in the increase of wool (which is estimated as 0.89 gram per day) is deducted from the total gain of nitrogen, the following numbers are obtained, indicating the amount of nitrogen deposited in the form of flesh:—

	Sheep 1.		Sheep 2.	
	Gram.	Per cent. of digested N.	Gram.	Per cent. of digested N.
1st period.....	1.29	3.91	1.15	3.51
2nd period.....	0.71	2.17	0.74	2.32
3rd period.....	0.73	2.26	1.21	3.74

	Sheep 3.		Sheep 4.	
	Gram.	Per cent. of digested N.	Gram.	Per cent. of digested N.
1st period.....	2.06	9.84	1.71	8.63
2nd period.....	—	—	—	—
3rd period.....	—	—	—	—

Apart from wool production, there was in the second period in Experiment II a complete nitrogen equilibrium, whilst, at the commencement, there was a daily gain of 1.88 gram of nitrogen, corresponding with 55 grams of flesh. In Experiment I with the lower nutritive ratio (1 : 2.3), there was a continuous deposition of nitrogen in the form of flesh. The experiments thus confirm the known fact that full-grown animals, fattened in the usual manner, very soon attain a nitrogen equilibrium as regards flesh; they also show that a continued slight production of flesh may occur with food richer in proteids. This was already observed by Maercker.

	Expt. 1.	Expt. 2.	Excess of Expt. 1 over Expt. 2.
Digested crude protein.....	202.44	123.11	79.33
„ ether extract.....	20.05	8.86	11.19
„ crude fibre.....	100.43	90.67	9.76
„ non-nitrogenous extract..	325.42	420.61	-95.19
Increase of live weight.....	71.5	62.5	9.0

The preceding table shows the average daily amounts of digested food compared with the average increase of live weight.

With regard to the observation that change of nitrogen increases after shearing and then gradually diminishes, it is remarked that experiments should not be commenced directly after shearing, but that the gradual increase in the amount of wool has no appreciable effect on the change of nitrogen. The loss of the wool seems to diminish somewhat the separation of nitrogen.

N. H. M.

Chemistry of the Kidney Substance. By L. LIEBERMANN (*Pflüger's Archiv*, 50, 55—56).—A very large proteïd constituent of the kidney substance is one similar to that found in the gastric mucous membrane, namely, a compound of lecithin and albumin, to which the term lecithalbumin is applied. It may be obtained as a residue after gastric digestion, and is stated to be acid in reaction.

W. D. H.

Asparagine as a Nutritive Substance. By G. POLITIS (*Zeit. Biol.*, 27, 492—506).—From experiments on rats, the following conclusions are drawn :—

1. A mixture of proteïd, fat, starch, and meat extract either with or without the addition of asparagine will keep the animals in a condition of equilibrium, or even increase the body weight.

2. Fat, starch, and meat extract alone soon produce death; addition of asparagine does not alter this result.

3. Asparagine has no influence on nitrogenous metabolism.

W. D. H.

Physiological Action of Asparagine. By J. MAUTHNER (*Zeit. Biol.*, 27, 507—517).—Experiments on dogs show that asparagine acts as a "proteïd-sparing" food in the same way as fats and carbohydrates may. There is, however, no evidence that it exercises this function from the synthesis of proteïd matter from the carbohydrate and asparagine given.

W. D. H.

Influence of Sugar on the Constitution of Milk Fat. By A. MAYER (*Bied. Centr.*, 21, 652—653; from *Milchzeit.*, 1892, 49).—The author recently brought forward the view that the composition of milk fat depends on the feeding, the greatest influence being shown by the soluble carbohydrates. In order to obtain experimental evidence, a six-year-old cow, which had calved about seven months previously, was fed for the week before the commencement of the experiments with the usual winter food, hay with linseed cake (2 kilos.). During the first period (November 17—26) and the third period (December 7—17), beet diffusion chips (32 kilos.), rye straw (5 kilos.), and linseed cake (4 kilos.) was given; in the second period (November 26—December 6), cane sugar (2 kilos.) in addition. The daily yield of milk was $11\frac{1}{4}$ litres (first period), $12\frac{1}{4}$ litres (second period), and $10\frac{1}{2}$ litres (third period). A table is given showing the melting point, solidifying point, and the amount of volatile acids in the butter in six different periods. The melting point was lowered by the use of sugar, and rose again in the third period. The amount of volatile acids rose during the second period (with sugar), but was

scarcely diminished at all in the third period. The influence of the sugar on the melting point of the solid fatty acids, separated by Reichert's method, is shown in the table:—

	1st period.	2nd period.	3rd period.
Melting point.....	43·7—43·8	41·4—41·7	42·3—42·4
Solidifying point..	37·6—37·7	35·3	36·5

The results explain the less consistency of Friesland butter as compared with Danish. N. H. M.

Melting Point and Composition of Butter from Cows variously fed. By A. MAYER (*Landw. Versuchs-Stat.*, 41, 15—35; compare Abstr., 1889, 173).—In the two series of experiments now described, one cow was used in each case. The feeding was changed every two weeks or less, and the sp. gr. and dry matter of the mixed morning and evening's milk determined, the fat being calculated by means of the Fleischmann-Morgen formula; the amount of volatile acids in the butter and the melting and solidifying points of the butter were also determined. These determinations were made 8—10 days after the commencement of each change of feeding, and again two days later. The daily yield of milk was also noted. The volatile acids of the butter varied with the first cow from 13·4 to 24·9; with the second cow from 20·1 to 32·2. The differences are less than those obtained in the earlier experiments, but are still considerable. When the differences of race, of individuals, and also differences in the period of lactation are combined with varying food, the extremes will differ still more widely. With regard to the bearing of this on the judgment of the adulteration of butter from the amount of volatile acids present, it is pointed out that the minimum number allowed for volatile acids is too high for some cases. On the other hand, the lower this number is fixed, the more adulterated butter will be passed over as pure. The only satisfactory manner of detecting adulteration will be to employ a combination of several methods.

The results show, in accordance with those of Nilson, that the period of lactation has some influence on the amount of volatile acids, higher numbers being obtained in the early periods than in the later ones. With regard to the relative effect of the different foods, the greatest depression was found in the case of poppy cake. Meadow grass in spring gave an increase when compared with the results obtained with hay and linseed cake, whilst autumn grass did not produce this effect, probably from its greater similarity to hay. Straw (pea and rye), instead of hay (in conjunction with linseed cake), caused a lowering of the acids from 24 to 16. Sour hay also caused a lowering in the amount of acids. The presence of lactic acid or volatile fatty acids in the food had no apparent action, at least in the small amounts employed. With regard to the manner in which the various foods act on the constitution, it frequently happened that a low amount of volatile fatty acids was obtained when the nutritive ratio of the food was low, and *vice versâ*, but this was not always the

case. It was generally found that the amount of acids varied with the amount of carbohydrates supplied, the greatest quantity of volatile acids being produced when the amount of carbohydrates, especially soluble carbohydrates, given in the food was greatest: thus beetroot was more favourable than hay, hay more favourable than sour fodder, for the production of volatile acids.

The melting and solidifying points of the butter do not always go together; the melting points fall as the period of lactation proceeds, whilst the solidifying points do not show this. Taking, however, the mean of the two temperatures in each case, the period of lactation has but little influence, whilst differences of race and individual show distinctly. As to the effect of different foods, it was found that pea straw and poppy cake taken together give high melting butter; next come straw and linseed or sesame cake, then earth-nut cake, and then cotton cake or rye. Soft butters, as compared with that obtained with the normal ration (hay and linseed cake), are produced by fresh meadow grass. Sour grass behaves in this respect much like hay. The addition of lactic or volatile fatty acids to the food somewhat lowered the melting point of the butter.

When the various foods are arranged in order showing the effect (1) on the amount of volatile acids, and (2) on the melting point of the butter, it is seen that those foods which produce the most acids generally produce the softest butter; but the rule is not without exceptions.

N. H. M.

Composition of Over-ripe Cheese. By A. MAGGIORA (*Exper. Stat. Record*, 4, 98—99; from *Arch. Hygiene*, 14, 216—224).—Three samples of gorgonzola were examined: No. 1 was soft and lardy, with an extensive growth of *Penicillium glaucum*, and contained a few maggots, and a greyish, soft liquid mass in the pores. No. 2 was very much changed, was viscous in many places, and had large numbers of maggots. No. 3 had been kept for about seven months in a stoppered bottle after it had become ripe; it was dark yellow, soft, viscous, and had a strong, caustic taste. When examined with the microscope, it was found that as the over-ripeness increased, the number of fat globules diminished, crystals of fatty acids, leucine, and tyrosine became numerous, and the number of bacteria, fungi, and insect eggs, &c., increased very materially. The following analytical results are given in percentages:—

	Dry matter.	Fat.	Total nitrogen.	Proteid nitrogen.	Amide nitrogen.	Nitrogen as ammonia.	Crude protein.	Proteids.	Ash less NaCl.	NaCl.
1...	65.59	37.52	4.28	2.59	1.01	0.68	26.75	16.20	2.74	1.33
2...	67.57	34.08	4.15	1.27	1.49	1.26	25.94	7.96	5.78	0.99
3...	62.37	36.19	4.31	0.58	1.88	1.86	26.94	3.63	9.55	0.92

The decomposition of the cheese is accompanied by the production of fatty acids from the fat and of amides and ammonia from the proteïds (paracaseïn). The cheese thus loses its nutritive properties until it may finally become mainly an aqueous solution of fatty acids (free or as ammonium salts), leucine, tyrosine, mineral salts, and a mass of bacteria and fungi.

N. H. M.

The Phosphates of Horse's Urine. By L. LIEBERMANN (*Pflüger's Archiv*, 50, 57—66).—The investigation relates to the phosphates normally present in horse's urine, and the changes that occur after excitation of the central nervous system by coitus, and in certain diseases of the spinal cord in these animals.

As the mean of nine observations on normal animals, the following numbers are obtained :—

Quantity of urine in 24 hours	3331 c.c.
Specific gravity	1·047
Total quantity of P_2O_5 in 24 hours . . .	0·2867 gram.
Percentage of P_2O_5 in urine	0·0098

Comparing with them the urine of 24 paralysed horses, no appreciable difference was found.

Coitus greatly increases the total quantity of urine and urea; the phosphoric acid is also increased, but not nearly so much in proportion. Only one experiment of this kind, however, was performed.

W. D. H.

Obstructive Jaundice. By V. HARLEY (*Brit. Med. J.*, 1892, ii, 397—402).—The following are the main conclusions arrived at from experiments on dogs :—

1. In obstruction of the bile ducts the bile is absorbed from the liver by the lymphatics, not by the blood vessels. This occurs even after the ligature of the thoracic duct by supplementary ducts which soon form.

2. After ligature of the common bile duct, the pent up bile becomes concentrated, especially in so far as its less soluble constituents (cholesterol and mucin) are concerned.

3. The animals not only lived, but often gained in weight, after ligature of the common bile ducts. Therefore the admission of bile into the duodenum is not essential to life.

4. Ligaturing the thoracic duct not only prevents the occurrence of obstructive jaundice after the occlusion of the common bile duct, but checks it even after it has set in.

W. D. H.

Transformation of the Albumin of the Urine in Bright's Disease. By E. GÉRARD (*J. Pharm.* [5], 26, 104—106).—The urine of a patient passed during 24 hours contained 10—16 grams of albumin when the milk treatment was commenced. Two days later, the urine contained no albumin coagulable by heat alone; but nitric acid gave an abundant precipitate, soluble in excess of the reagent. A saturated sodium chloride solution caused an abundant flocculent precipitate, which the addition of acetic acid still further increased. These

various reactions are characteristic of propeptones. Further, it was possible to discriminate between the different compounds which according to Kühne make up the propeptones thus:—Heteroalbumose and protalbumose, precipitable by sodium chloride, and deutoalbumose, only precipitable by excess of ammonium sulphate. To determine the amount of propeptone contained in this urine, acetic acid is added, and an excess of sodium chloride; about 24 hours afterwards there is added to the solution one-tenth its weight of ammonium sulphate. The precipitate is washed with water containing a little sodium chloride and ammonium sulphate. The propeptones thus separated are redissolved in water acidified by acetic acid, precipitated by absolute alcohol, dried, and weighed. At the beginning of the milk treatment, about 6·5—7 grams of propeptones was secreted in 24 hours, later this diminished to 1·9—2·6 grams. After some time, the patient was fed with yolk of egg, then ordinary food. The urine never contained albumin coagulable by heat, but always propeptones. Hence under the milk treatment, the albumin of urine in Bright's disease can be replaced by albumin partially digested. Further it is not sufficient to seek only for albumin coagulable by heat; it is equally necessary to examine for other albuminous principles, and amongst others the propeptones which are formed under the lactic treatment, and whose presence indicates phases of the pathologic state.

J. T.

Phloridzin Diabetes. By M. CREMER and A. RITTER (*Zeit. Biol.*, 27, 459—465).—Experiments on hens and rabbits are recorded, which show that diabetes may be induced, not only by feeding animals on phloridzin or phloretin, but also by subcutaneous injection of these substances. The sugar appears to originate chiefly from proteid metabolism. The close interdependence of this subject with glycogen formation is pointed out, and the rabbit is recommended as a suitable animal for working out this question more fully.

W. D. H.

Pancreatic Diabetes. By V. HARLEY (*Brit. Med. J.*, 1892, ii, 451—454).—The view advanced by Lépine that the sugar in the urine of patients suffering from pancreatic diabetes is due to the absence of a glycolytic pancreatic ferment in the circulation is accepted. Certain toxic symptoms (tissue waste and muscular weakness) are considered to arise from the retention in the organism of certain excrementitious substances (leucomaines).

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Difference between Formed and Unformed Ferments. By M. ARTHUS and A. HUBER (*Arch. de Physiol.*, 1892, 651—663).—Sodium fluoride, to the amount of 1 per cent. of the solution, kills all living things, and thus stops fermentations caused by micro-organisms. It does not stop fermentations caused by enzymes.

W. D. H.

Influence of Antiseptics on Fermentation. By E. BIERNACKI (*Pflüger's Archiv*, 49, 112—140).—All antiseptic agents have the property, under certain conditions, especially in small doses, of increasing alcoholic fermentations. The more powerful the antiseptic properties, the more powerful also is this action. The increase in alcoholic fermentation, and the same is true for fermentative and putrefactive processes generally, occurs with larger doses if very large quantities of the fermentable substances are present also. Organic substances appear to have the power in question to a greater degree than those of inorganic nature, and the richer an organic compound is in carbon, the more powerful it is. Among benzene derivatives, the greater the number of hydroxyl atoms, the weaker is the antiseptic, both as regards its antisepticity and its power in small doses of accelerating the fermentation. A mixture of antiseptics increases anti-fermentative action. The combination of organic with inorganic compounds is more powerful than a mixture of organic substances. W. D. H.

The Power of Propagation of the Leguminous Bacteria in Soil. By F. NOBBE, E. SCHMID, L. HILTNER, and E. HOTTER (*Landw. Versuchs-Stat.*, 41, 137—138).—It was repeatedly observed that root nodules produced by inoculation from above only developed on the upper portions of the roots. This may be due to a want of sufficient oxygen in the subsoil, or to the inability of the organisms to reach the subsoil. To clear up this point, five peas were planted on 16th May, in non-nitrogenous and sterilised soil (with minerals); and on 26th June, after nitrogen hunger had commenced, were inoculated with an emulsion of pure cultures of pea-nodule bacteria (5 c.c. for each plant) at a depth of 200 mm. By the 20th July, the plants no longer showed nitrogen hunger, and on the 31st four of the dark-green plants (1150 mm. high) had 14—16 leaves, 1—2 pods, and 2—4 flowers. The fifth plant was somewhat behind the others. When taken up (2nd October) nodules were found only on the lower roots (both on roots of the second and first order) where inoculated. The upper parts of the roots were quite free from nodules. In a second experiment, in which the infecting material was introduced into the centre of the pot about 120 mm. deep, the result was similar, the nodules forming on the corresponding portion of the root. A similar result was obtained by infecting the upper and lower portions: the intermediate parts of the root remained free from nodules.

The nodules are generally situated on roots of the first and second order; in the case of late infection, on roots of the third order. It is the young roots which are capable of being infected, so long as they have susceptible hairs. This explains why late infection at the surface is often without effect. The age of the plant, provided that the roots are normal, has nothing to do with nodule formation. There seems to be no rule as to the position of the nodules, apart from the presence of the nodule organisms. N. H. M.

Assimilation of Formaldehyde by Green Plant Cells. By T. BOKORNY (*Chem. Centr.*, 1892, ii, 80; from *Landw. Jahrb.*, 21, 445—465).—It is shown that plants which have been deprived of starch, and placed in an atmosphere freed from carbonic anhydride, are capable

of forming considerable quantities of starch if fed with the sodium hydrogen sulphite compound of formaldehyde, and placed in a strong light. In the dark, no conversion of formaldehyde into starch takes place.

C. F. B.

Carotene. By O. HESSE (*Annalen*, 271, 229—230).—In the author's opinion the colorimetric method employed for the detection of carotene in plants is not a satisfactory one, inasmuch as other coloured compounds of like behaviour, such as rubidin, doubtless occur in the green parts of plants.

F. S. K.

The Physiological Meaning of the Root Nodules of *Eleagnus angustifolius*. By F. NOBBE, E. SCHMID, L. HILTNER, and E. HOTTER (*Landw. Versuchs-Stat.*, 41, 138—140).—Various experiments were commenced in 1891 to ascertain the physiological meaning of the root nodules of various non-leguminous plants (*Eleagnus*, *Hippophæ*, and *Alnus*). *Eleagnus* sprouts were planted in two pots containing sterilised nitrogen-free sand; the one pot, a week afterwards, was infected with an extract of *Eleagnus* soil. The infection had no visible effect during the whole summer, but in the autumn, one of the plants began to acquire a somewhat fresher green colour than the others, and in the spring of the following year this plant was unmistakably more vigorous than the others; it was strong and had side shoots. All the plants (of both pots) were isolated in nitrogen-free sand, when it was seen that only the plant which was benefited by the inoculation had nodules. On the 5th of September the main stem of this plant was 530 mm. high with 54 leaves and three side shoots 350, 325, and 105 mm. long. The non-infected plants and those which were unsuccessfully infected had an average height of 140 mm., were scanty and without side shoots. Only one of the infected plants began to get greener in July, 1892; it had three small oblong nodules when taken up.

There is no doubt that *Eleagnus* is enabled by the possession of nodules to utilise free atmospheric nitrogen. The organisms which produce these nodules were obtained in pure cultivations and are totally different from *Bacterium radicicola*.

N. H. M.

The Nitrogen Question. By A. PETERMANN (*Mém. Acad. roy. Belg.*, 47, 1892; compare Abstr., 1890, 816).—The first series of experiments now described were made with haricots and barley; each experiment consisted of four pots each with three haricot or six barley plants, the produce and sand of the four being mixed at the end of the experiments. The pots were kept in a glass-house and watered with well-water, which was analysed from time to time. In each case there were two experiments with sand alone, microbe-seeded with soil extract (1 and 1'); and two with sand, mineral manure, and microbe-seeded (2 and 2'). Each pot contained 4·5 kilos. of sand (containing 0·000633 nitrogen per cent.), that is, 18 kilos. for each experiment.

The haricots grew well and flowered, but those in the pots to which minerals were applied were stronger and greener than the others. The barley of the mineral pots grew well and produced ears; those

grown without minerals remained small and soon became yellow. The roots of the haricots had nodules, but they were much smaller than the lupin nodules.

The following amounts of dry matter (tops and roots) were produced in each experiment of four pots :—

	1.	1'.	2.	2'.
Haricots	15.70	16.68	28.06	29.8
Barley	15.50	16.93	57.14	45.42

The nitrogen was determined in the soil, seeds, and water as used, and in the soil and produce at the end of the experiments. The results are given in the table on p. 35.

An experiment was made simultaneously with those just described in which two more pots, each with 4.5 kilos. of sand, were exposed to air, being kept moist the whole time. The nitrogen of the sand and water amounted, in each case, to 0.0333 gram; at the end of 103 days 0.0247 and 0.0283 gram was found, being a loss of 0.0086 and 0.0050 gram of nitrogen respectively.

The experiments confirm the earlier ones (*loc. cit.*) in which lupins were shown to acquire nitrogen from the air. They also show a gain of nitrogen from the air in the case of barley, which is non-leguminous and has no nodules. The author concludes, therefore, with Frank,* that root nodules are not a general cause of nitrogen fixation, but assist in special cases.

The second series of experiments was made to ascertain whether the gain of nitrogen was due to the free or the combined nitrogen of the air. For these experiments, the tanks, or pits, employed in the earlier ones (*loc. cit.*) were used, but were now covered with a glass case 7.2 m. long, 1.2 m. wide, and of an average height of 1.1 m. This was divided into six compartments, one for each pit, each carefully isolated. There was also an arrangement for watering, and an aspirator, by means of which air could be made to pass through the cases. Nos. 1, 2, and 3 had ordinary air, Nos. 4, 5, and 6, air freed from nitrogen compounds. The pits contained each 1 cub. m. of sand weighing 1435 kilos. and containing 0.000228 per cent. of nitrogen and the necessary minerals; 250 c.c. of soil extract was also given. The following seeds were sown :—pits 1 and 6, 26 haricots; pits 2 and 4, 72 barley; pit 3, 45 lupins and pit 4, 36 lupins.

The plants developed well; the haricots and lupins flowered and produced seed, and the barley grew to the height of the cases. When the plants were taken up, the surface of the sand was found to be partially covered with chlorophyllous algæ. The roots of the haricots

* In a criticism of Frank's paper "On the Assimilation of Free Nitrogen," &c. (Abstr., 1892, 270), Kreisler points out (*Bied. Centr.*, 21, 257) that Frank's method of analysis was not sufficiently exact to justify this conclusion (that non-leguminous plants fix free nitrogen), or any other. Thus, the small differences in the percentages of nitrogen in the soil at the beginning and end of the experiments, when calculated on the amounts of soil analysed (7—9 grams), become extremely small, quite within the unavoidable error of experiment. On the other hand, this small gain, when calculated on the total soil employed, becomes very great, far greater than the gain of nitrogen in the produce. There is, therefore, no reason why the plant nitrogen should not be assumed to have been derived from the soil.—N. H. M.

TABLE I.—*First Series*

Nitrogen (in grams).								
At commence- ment.	At conclusion.					Gain.		
	In soil.			In produce.	Total.			
	Organic.	As ammonia.	Nitric.				Total.	
<i>Haricots.</i>								
1.....	0·2438	0·0671	0·0156	0·0234	0·1061	0·4141	0·5202	0·2764
1'.....	0·2438	0·0611	0·0156	0·0156	0·0923	0·4000	0·4923	0·2485
2.....	0·2462	0·0691	0·0091	0·0221	0·1003	0·4904	0·5907	0·3445
2'.....	0·2462	0·0611	0·0120	0·0192	0·0923	0·4672	0·5595	0·3133
<i>Barley.</i>								
1.....	0·1950	0·0691	0·0156	0·0338	0·1185	0·3288	0·4473	0·2523
1'.....	0·1950	0·0550	0·0234	0·0052	0·0836	0·3027	0·3863	0·1913
2.....	0·2344	0·0601	0·0117	0·0169	0·0887	0·4973	0·5860	0·3516
2'.....	0·2344	0·0550	0·0117	0·0169	0·0836	0·4218	0·5054	0·2710

* The nitrogen of the soil was 0·1140 gram in each case. The nitrogen in the seeds was : haricots, 0·0624; barley, 0·0120 gram.

TABLE II.—*Second Series.*

Nitrogen (in grams).						
At commencement.				At conclusion.		
In soil* and water.	Seeds.	Total.	Soil.	Drainage.	Produce.	Total.
<i>Haricots.</i>						
1.....	3·4311	3·6180	5·1115	0·0509	0·9017	6·0641
6.....	3·4311	3·6180	4·6681	0·0697	0·6979	5·4357
						2·4461 1·8177
<i>Lupins.</i>						
3.....	3·5074	3·9134	5·8562	0·0189	6·6898	12·5649
4.....	3·5074	3·8321	5·5248	0·0158	8·0756	13·6162
						8·6315 9·7841
<i>Barley.</i>						
2.....	3·4494	3·4858	6·0227	0·0389	1·0416	7·1032
5.....	3·4494	3·4858	5·7443	0·0555	1·0572	6·8570
						3·6174 3·3712

* The amount of nitrogen in the soil was in each case 3·2756 grams.

had nodules from the size of a pin's head to that of hemp seed; the lupin nodules were sometimes as large as a hazel nut.

The following table shows the amount of dry produce (in grams) from each of the three pits, (1) with ordinary air, (2) with air freed from combined nitrogen:—

	Haricots.	Lupins.	Barley.
1. (Pits 1, 3, and 2).....	29·06	267·72	94·38
2. (Pits 6, 5, and 4).....	23·15	352·64	94·03

The nitrogen results are given on p. 36.

The nodules (dried) of the two lupin pits weighed, respectively, 6·37 and 8·00 grams, and contain 4·591 and 4·490 per cent. of nitrogen.

The whole of the results taken together prove the intervention of atmospheric nitrogen, not only in the case of lupins and haricots, but also in that of barley, and in those of the second series, prove further that the gain depends essentially on the fixation of elementary nitrogen. At the same time, the intervention of combined nitrogen is manifest in the results obtained with haricots and barley.

In conclusion, the author considers that if the difference of his results from those of Boussingault and all his successors who employed ignited soil gives rise to the idea of ascribing the utilisation of free nitrogen to intervention of soil micro-organisms, even in the case of the Gramineæ, it must be recognised that it is by no means proved that reactions of another kind do not take place, as, for instance, the direct assimilation of nitrogen by vegetable cellulose, which was certainly insufficiently demonstrated by Ville, but which received strong support from Frank's results (see footnote, p. 34). To clear up this point, it will be necessary to grow barley in sterilised, and in infected soil in an atmosphere free from combined nitrogen.

N. H. M.

Chemical Composition of Apples and Pears, especially with regard to their Utilisation for Fruit Wine. By P. KULISCH (*Bied. Centr.*, 21, 700—702; from *Landw. Jahrb.*, 1892, 427).—The examination of a large number of varieties of apples showed that the amount of cane sugar varies both absolutely and in relation to the amount of invert sugar. When the apples are detached from the tree, cane sugar continues to be produced from the starch present, but, finally, the cane sugar becomes almost completely converted into directly reducing sugar. There is no relation between the amount of cane sugar and acid, and a high percentage of acid does not result in a lower percentage of sugar. The suitability of a particular kind of fruit for wine depends on other properties besides the amounts of determinable constituents, the knowledge of which is chiefly of use in mixing the various kinds of most. Addition of water or sugar with a view to improving most is to be avoided. 5·5—6 per cent. of alcohol is sufficient for fruit wine.

There seems to be no relation between the fertility of the trees and the percentage of sugar in the fruit, although the number of apples has great influence on the weight of the single apples. Large apples

contain, however, a greater percentage of sugar than small apples from the same tree.

With regard to the presence of cane sugar in pears, the author found, contrary to his early results, sugar in those which had been kept to ripen; this requires further investigation.

Currants, gooseberries, blackberries, and mulberries contain only traces of cane sugar, whilst most stone fruits contain much. No considerable amount of cane sugar could be found in raspberries and bilberries.

N. H. M.

Chemistry of the Tobacco Plant. By R. J. DAVIDSON (*Exper. Stat. Record*, 4, 30—31; from *Virg. Stat. Bul.*, No. 14, 1892).—The following table shows the average percentage amounts of dry matter, nitrogen, and ash-constituents in the air dried leaves, stems, and roots of four varieties of tobacco:—

	Dry matter.	Nitrogen.	P ₂ O ₅ .	K ₂ O.	CaO.	MgO.	Insoluble matter.
Leaf.	92·38	4·37	0·502	5·738	5·449	0·956	1·943
Stem	93·82	3·71	0·646	5·020	2·222	0·593	0·662
Root	93·75	1·88	0·211	1·777	1·277	0·208	2·877

With regard to the relative amounts of leaf, stem, and root, the averages for all four varieties are respectively 55, 21·9, and 23·1 per cent. A crop yielding 1000 lbs. of leaves would contain an average amount of 66·85 lbs. of nitrogen, 8·68 lbs. of phosphoric acid and 85·41 lbs. of potash distributed as follows:—

	N.	P ₂ O ₅ .	K ₂ O.
In leaves.....	43·7 lbs.	5·0 lbs.	57·4 lbs.
In stems.....	15·2 „	2·7 „	20·5 „
In roots	7·9 „	1·0 „	7·5 „

About one third of the fertilising constituents are, therefore, in the roots and stems, which should be returned to the soil.

N. H. M.

Manufacture and Composition of Linseed Cake and Meal. By HASELHOFF (*Landw. Versuchs-Stat.*, 41, 55—72).—Flax is chiefly grown in Germany for the flax; for seed it is almost only grown in Mecklenburg and Königsberg, and the seed is not of very good quality for the production of oil. The American seed is of about the same quality; the Indian (Bombay) is better, whilst the best seed is that from Russia, especially South Russia. Most of the impurities are removed by sifting; when there remains only 4 per cent. of foreign matter (or even 8 per cent. if the foreign matter consists of oily seeds), the seed is practically pure. With regard to the manufacture of linseed oil, the original method consisted in pounding the seeds. Now there are two methods by which the oil is pressed out; in the one heat is applied to the vessel containing the seeds (either by direct firing or

steam), in the other the seed is directly treated with superheated steam. Another method is to extract with light petroleum. The residue (cake or meal) varies in composition according to the method employed. Thus, whilst the residue from pressed seeds contains about 32—36·4 per cent. of protein and 9—11 per cent. of fat, the residue from extracted seeds contains more proteïds (40 per cent.) and less fat (3—4 per cent.). The amount of mucilage also varies; where direct steaming is employed the amount is diminished, and cake so obtained will keep for years without becoming mouldy. This is also the case with cake prepared by the light petroleum method, but this seems to be due, not to the abstraction of mucilage, but to the action of the light petroleum.

For adulteration, not only vegetable substances but also heavy spar, gypsum, chalk, and salt are employed; saw-dust has been found. Rape-cake meal may be detected by stirring in water in a glass cylinder and allowing to settle; if any dark particles are visible, rape is probably present. A few drops of aqueous alkali will give an intense yellow colour if rape is present. Amygdalin does not seem to be actually injurious, but mustard, corn-cockle, and *Camelina* are said to be injurious, whilst castor oil is poisonous and may cause death. Vegetable impurities can mostly only be detected microscopically and the amounts only approximately estimated. But the amount of fat, and especially of protein, give a good idea as to purity or otherwise. When mineral impurities are present they may be detected by the amount of ash, which generally should not exceed 5 per cent. Cake containing over 14 per cent. of water cannot be considered as pure.

With regard to fat, it should be noted what results are obtained when the substance is (1) not previously dried, (2) when dried for two hours at 100—105°, and (3) when dried for two hours at 100° in an atmosphere free from oxygen; the results should not differ. The rancidity of the fat is determined (1) after the fat has been so long dried that it no longer has an unpleasant odour, and (2) without previous drying. The first estimation gives a lower result than the second, from loss of volatile fatty acids. The higher the percentage of acid the greater the difference in the two experiments; the estimation of rancidity of linseed residues and in foods generally should therefore be made in the fat from undried substance. The cake and meal were also examined bacteriologically; large numbers of micro-organisms were found, but the results give no indication of the quality of the substance examined, as the nature (injurious or otherwise) of the micro-organisms is not known. N. H. M.

Manufacture and Impurities of Linseed Cake. By F. J. VAN PESCH (*Land. Versuchs-Stat.*, 41, 73—93).—Only very little of the linseed worked in Holland is produced in that country; much is obtained from Russia, but most from India. The composition of samples of cake examined at Wageningen varied as follows: proteïds (22—37), fatty matter (6·2—18·5), starchy matter (30), water (11—16), ash (4·5—8·6), and crude fibre (7·3—12·3 per cent.). The average amount of digestible matter (according to Kühn) would

therefore be:—proteïds 26, fatty matter 10·4, and starchy matter 24·3 per cent. The origin of the seed has a great influence on the quality of the cake. According to Voelcker, the Russian seeds contain most albumin; those grown further south contain the most fat. The method for the microscopic examination of linseed was described by Kobus, (*Landw. Jahrb.*, 1884, 120). The chief weeds which occur in linseed are *Polygonum convolvulus* and *lapathifolium*; rape is very frequent, whilst *Camelina dentata*, *Galium aparine*, *Thlaspi arvense*, and *Agrostemma githago* also occur. Less frequent are *Brassica nigra*, *Sinapis arvensis*, *Plantago lanceolata*, *Lolium*, and other grasses. Besides these seeds which occur naturally, stalks and sand are sometimes found. In Belgium rice meal and earth-nut skins are frequently added.

Cake manufactured by the so-called American method, in which the finely-powdered seed is extracted by carbon bisulphide, only contains 3—4 per cent. of fatty matter, and is therefore not used in Holland. The method employed for the examination of cake is as follows. The sample is made to pass through a 5 mm. sieve, and 5 grams stirred in a beaker with 100 c.c. of boiling water. Beakers of one size are employed, so that the more or less swelling of the powdered cake and the smaller or greater amount of liquid which separates can be compared. It is also noticed whether the liquid is quite thin or whether it is slimy. With regard to the swelling up, *Camelina* swells considerably more than linseed. Kobus (*loc. cit.*) found that 1 gram of linseed kept in water for one hour weighed 2·7—2·8 grams, whilst 1 gram of *Camelina* weighed 4·4 grams after the same treatment. A part of the liquid is tested with iodine for starch; only a light blue colour should be produced. The residue obtained when the water is poured off is examined microscopically (Kobus, *loc. cit.*). The number of foreign particles is estimated in 5 grams, the separation being effected by a jet of water on the substance in a 1·2 mm. sieve. Determinations of proteïds, fat, and ash are also made.

The injurious substances sometimes found in linseed cake are corn-cockle, containing a poisonous substance, saponin or githagin, the seeds of *Thlaspi arvense*, which, when eaten by cows, impart a garlic-like taste to the milk, and hemp seed, which causes diarrhœa. Barium sulphate is objectionable, whilst salt, besides being good for cattle, has the advantage of making the cake softer; on the other hand, the cake becomes quickly moist and therefore spoils. The poisonous action of castor oil beans was first shown by van den Berghe. Other substances doubtless occur which are more or less poisonous or injurious when much of them is present.

The results of experiments made at Wageningen show that in 5 grams of substance it requires only 16 seeds of *Polygonum lapathifolium*, 13 of *P. convol.*, 4 of *Galium aparine*, and 46 of *Camelina* to make 1 per cent. of the cake. Each seed is reckoned as follows:—*Camelina* 2, *Polygonum lap.* 6, *P. convol.* 8, *Galium aparine* 25; if the sum of the numbers found exceeds 100, the cake is not pure enough.

In most cases it is sufficient to magnify 70—80 times, but in some cases 300 times. For the detection of very finely-powdered substances in cake, a test tube is half filled with the powdered cake, treated with

alcohol, well shaken, and allowed to settle; the alcohol is poured off and some of the fine meal which floats on it put on an object glass. The alcohol is evaporated, a drop of glycerol and aqueous soda added and pressed with a second glass. When magnified 300 times, earth-nut meal is readily distinguished; it is seen as ring-shaped depressions. Other substances than earth-nut meal can only be detected by special methods.

N. H. M.

Analytical Chemistry.

Improvements in Gasvolumeters. By G. LUNGE (*Ber.*, 25, 3157—3164).—Arrangements are here described for closing the "reduction tube" of the gasvolumeter (*Abstr.*, 1890, 660) other than by the use of a stop-cock or by sealing the end, both of which methods have certain disadvantages. By suitably adjusting the levels of the mercury in the "reduction" and "measuring" tubes, it is possible to employ the instrument for the measurement of both moist and dry gases, as also to use it as a "gravivolumeter" (compare Japp, *Trans.*, 1891, 894; Lunge, *Proc.*, 1891, 170).

A. R. L.

Titration Apparatus with Automatic Zero Adjustment. By S. KRAWCZYNSKI (*Ber.*, 25, 3010—3011).—Into one neck of a two-necked Woulff's bottle of suitable capacity is fixed by means of a cork, a burette consisting of an inner and outer tube; and to the other neck of the bottle is fastened a small, two-bladder hand bellows and a side tube for releasing the air pressure after the burette is filled. The inner tube of the burette is open at both ends, reaches nearly to the bottom of the Woulff's bottle, and ends about 5 cm. below the top of the outer tube, this point being the zero mark. The outer tube, fused on to the inner tube just above the cork, is graduated, and has an ordinary burette tap fused into the side near the bottom.

E. C. R.

Estimation of Free Acids in the presence of Acid Phosphates. By J. WAGNER (*Pflüger's Archiv*, 50, 375—384).—Leo's method (*Abstr.*, 1891, 1288) is again criticised and declared to be wholly worthless.

W. D. H.

Estimation of Chlorine in Electrolysed Solutions. By L. M. NORTON (*Chem. News*, 66, 115—116).—For the estimation of total chlorine and chlorine as chloride, hypochlorite, and chlorate in electrolysed or other solutions, the author mentions various methods, but regards the following mode of procedure as most convenient. The chlorine present as hypochlorite is estimated by titration with sodium arsenite in the usual manner, then by titrating an aliquot part of the same solution with silver nitrate, and deducting the chlorine present as hypochlorite from the result, the amount of chlorine present as chloride is found. The total chlorine is estimated in a fresh portion by treat-

ing it with saturated aqueous sulphurous acid to reduce chlorate, and employing Volhard's method of adding excess of standardised silver nitrate, and titrating back with ammonium thiocyanate in the presence of ferric alum. The difference between this result and the sum of the chlorine present as chloride and hypochlorite gives the amount present as chlorate.

D. A. L.

Estimation of Bromine and Iodine in presence of Chlorine.

By E. NIHOUL (*Zeit. angew. Chem.*, 1891, 441).—The author has attempted to substitute hydrogen chloride for chlorine in the well known indirect process of determining the amount of the three halogens when precipitated as silver salts. Silver bromide is completely converted into chloride when heated for an hour in a current of hydrogen chloride, but unfortunately silver iodide is but partially decomposed, and as the action of chlorine is complete in about 10 minutes, the author is not inclined to give up the use of that gas.

L. DE K.

Estimation of Nitrogen in Nitrates. By ALBERTI and HEMPEL (*Zeit. angew. Chem.*, 1891, 398—400).—Fricke (compare Abstr., 1892, 527) strongly recommended Ulsch's process for the estimation of nitrogen in nitrates. The authors have also investigated the method, and as the results of numerous experiments, now propose its universal introduction in agricultural chemical stations. Their test analyses, practised not only on pure and commercial nitrates, but also on complex manures, are very satisfactory.

L. DE K.

Estimation of Nitrogen in Nitrates. By K. ULSCH (*Zeit. angew. Chem.*, 1891, 719).—The success of the author's process depends, of course, greatly on the accurate estimation of the ammonia obtained by reducing the nitrate by means of sulphuric acid and metallic iron. The author now puts into the receiver a quantity of N/5 acid slightly insufficient to neutralise all the ammonia which is given off on distilling the liquid with excess of sodium hydroxide. More acid is then carefully added until exact neutrality is obtained. The results thus obtained are more trustworthy than those got by the usual procedure of using excess of acid, and then titrating back with alkali.

L. DE K.

Iodometric Estimation of Nitrates. By F. A. GOOCH and H. W. GRUENER (*Amer. J. Sci.*, 44, 117—123).—The authors recommend distilling the nitrate (about 0.2 gram) with 20 c.c. of a saturated solution of crystallised manganous chloride in strong, hydrochloric acid, in a current of carbonic anhydride. The products of the distillation are passed into a solution of potassium iodide, and the liberated iodine is afterwards titrated by means of sodium thio-sulphate. 3 mols. of iodine correspond with 2 mols. of hydrogen nitrate.

The apparatus employed consists of a bent pipette, serving instead of a retort, which is connected with a Kipp's apparatus evolving carbonic anhydride. The other goose-neck like end is sealed to a Will and Varentrap nitrogen bulb, the exit tube of which is drawn out, so that it may be pushed well within the inlet tube of a Will and

Varrentrap absorption flask. A third receiver simply acts as a trap to exclude air from the absorption apparatus proper. The titration should be completed immediately after the distillation, during which the nitrogen bulbs should be immersed in cold water; otherwise, traces of dissolved nitric oxide might get oxidised and liberate more iodine. The test analyses are very satisfactory. L. DE K.

Estimation of Nitrous Acid in Sodium Nitrate. By O. REITMAIR and A. STUTZER (*Zeit. angew. Chem.*, 1891, 666—667).—The authors have come to the conclusion that the estimation with potassium permanganate gives erroneous results, and that for accurate determinations, Lunge's process should be adopted (compare Abstr., 1892, 1029). L. DE K.

Determination of Nitrogen in Soils by Kjeldahl's Method. By J. A. MULLER (*Ann. Chim. Phys.* [6], 22, 393—401).—A number of comparative determinations have shown that when the nitrogen in soils is estimated by Kjeldahl's method, the results come out, as a rule, a little lower than when the soda-lime process is employed; the difference is, on the average, 0.04 gram of nitrogen per kilo. of dry soil. It is necessary, however, to add a little benzoic acid to the mixture of soil and fuming sulphuric acid; otherwise the results may fall out much too low.

The apparatus employed by the author consisted of a small, long-necked flask, of about 75 c.c. capacity, heated in an air-bath; the neck of the flask, projecting from the air-bath, was bent downwards and introduced into a small flask, so that any sulphuric acid which was volatilised during the process would not run back down the sides of the hot vessel and cause fracture.

The proportions taken were:—15 grams of the dry, finely-divided soil, 30 c.c. of fuming sulphuric acid, and about 0.3 gram of benzoic acid. The operation occupies about 12 to 18 hours, during which time the temperature is gradually raised; towards the end of the operation, the mixture is heated sufficiently to distil about 1.5 c.c. of the sulphuric acid.

The soils examined were free from, or contained only traces of, nitrates. F. S. K.

Estimation of Phosphorus in Steel. By H. WDOWISZEWSKI (*Chem. Centr.*, 1892, ii, 56—57; from *Stahl u. Eisen*, 12, 381).—The following combination of hitherto known methods is proposed; it is asserted that an accurate estimation can be made in two hours. 2—5 grams of steel is dissolved in 30—75 c.c. of nitric acid (sp. gr. 1.2) in a conical flask of 300—500 c.c. capacity, the boiling solution is treated with 10—25 c.c. of a 1 per cent. permanganate solution, and boiled until the precipitated manganese dioxide rapidly sinks to the bottom, when the flask is removed from the flame. 2 c.c. of concentrated hydrochloric acid is now added for every gram of steel taken, and the boiling is continued until the dioxide has completely dissolved, and all the chlorine is driven off. The solution is then treated with strong ammonia in considerable excess, being shaken

continually the while, and to the gelatinous mass strong nitric acid is added little by little in quantity more than sufficient to dissolve the precipitate. The solution is then heated to 85° , 25—30 c.c. of ammonium molybdate is added, and the flask is stoppered and shaken gently, the stopper being removed occasionally, and, finally, wrapped in a cloth and shaken violently for five minutes. The precipitate is collected with the aid of the pump, washed with 15 per cent. ammonium nitrate, and then 2—3 times with water, brought, together with the filter, into a flask, and treated with 6—10 c.c. of an ammonia solution standardised against phosphorus. After the precipitate has dissolved, the excess of ammonia is determined by titration with an equivalent solution of hydrochloric acid. The burettes used were graduated in $1/30$ c.c.; 1 c.c. of the ammonia solution = 0.03534 per cent. of phosphorus.

C. F. B.

Estimation of Phosphorus in Steel and Cast Iron. By R. ZIMMERMANN (*Chem. Centr.*, 1892, ii, 131—132; from *Stahl u. Eisen*, 12, 524—527).—A modification of Metz' method, occupying 30—35 minutes for steel, and two hours for cast iron, as in the latter case silica and graphite have to be separated. 5.0008 grams of the metal is dissolved in a tall beaker in nitric acid (sp. gr. 1.20), oxidised with permanganate, the manganese dioxide reduced with hydrochloric or oxalic acid, the clear solution treated with ammonium nitrate, and the phosphorus precipitated by a large excess of molybdate solution. After shaking for a few minutes, the beaker is inclined, the precipitate allowed to settle, and, after 15—20 minutes, the clear solution siphoned off. The precipitate is washed on a filter of 6—7 cm. diameter with dilute nitric acid of sp. gr. 1.002, then washed with this solution through a small funnel into a specific gravity bottle, which is filled and weighed (G = bottle + precipitate + solution). g (= bottle + solution) is then read off from a table, and $\frac{1}{2}(G - g)$ gives the percentage of phosphorus.

C. F. B.

Rapid Estimation of Phosphorus in Iron, Steel, and Ores. By J. O. HANDY (*Chem. Centr.*, 1892, ii, 185; from *J. anal. Chem.*, 6, 204—211).—The method is based on the fact that precipitated ammonium phosphomolybdate, when freed from acid by washing with a neutral solution of potassium nitrate, is dissolved by standard soda, the excess of which may be determined by titration with nitric acid, phenolphthalein being used as an indicator. 2 grams of steel is dissolved in 75 c.c. of nitric acid (sp. gr. 1.13) in a conical flask, 15 c.c. of 0.5 per cent. permanganate solution added to the boiling solution, the whole boiled, about 0.03 gram of cane sugar added, and heated until the manganese peroxide has dissolved. The flask is then removed from the flame, 13 c.c. of ammonia (sp. gr. 0.90) is added, the whole is shaken, cooled to 85° , treated with 50 c.c. of molybdate solution, shaken for five minutes, and the precipitate collected, washed with 0.1 per cent. nitric acid, and then five times with 0.1 per cent. potassium nitrate solution. The filter and precipitate are then put back into the flask, 20 c.c. of standard soda, water,

and phenolphthaleïn are added, and the excess of soda titrated with nitric acid.

The molybdate solution is prepared by dissolving 1 lb. of molybdic acid in 1200 c.c. of water and 700 c.c. of ammonia (sp. gr. 0·9), adding 300 c.c. nitric acid (sp. gr. 1·42), and pouring the mixture, a quarter at a time, into four flasks each containing a mixture of 500 c.c. of nitric acid (sp. gr. 1·42) and 1200 c.c. water; no molybdic acid is precipitated. The soda and nitric acid solutions are standardised with pure, yellow ammonium phosphomolybdate containing 1·63 per cent. phosphorus. 0·014 per cent. of arsenic in the iron does not affect the determination of the phosphorus.

C. F. B.

Precipitation of Phosphates and Arsenates by Ammonium Molybdate. By B. MOREAU (*J. Pharm.* [5], 26, 157—163).—The reagent is prepared by dissolving 12 grams of ammonium molybdate in 10—15 grams of warm water; to this is added a mixture of 145 grams of nitric acid and 30 grams of water. The solution is heated on the water-bath from 10 to 15 minutes, made up to a litre, and decanted after settling for some hours. In testing for phosphate or arsenate, 2 c.c. of the reagent is heated to boiling in a tube, taking care not to heat the surface, then some drops of the solution to be tested are added, boiled again if necessary, when a precipitate indicates a phosphate or an arsenate. 1 gram of phosphoric acid in 10 litres of water is faintly indicated, and 1 gram of arsenic acid in 1300 grams of water. Quantitatively, 60 c.c. of the reagent is heated nearly to boiling on the water-bath; it should remain clear, then 5 c.c. of nitric acid is added, 20 c.c. of the solution of phosphate or arsenate containing about 1 per cent., and, finally, 6—8 grams of ammonium nitrate crystals; it is then boiled for a quarter of an hour with frequent shaking.

J. T.

Estimation of Carbon in Iron or Steel, also of Carbonic Acid in Aqueous Solutions. By G. LUNGE and L. MARCHLEWSKI (*Zeit. angew. Chem.*, 1891, 412—414).—The authors (compare Abstr., 1892, 531) state that by using a larger flask and funnel, their apparatus is very suitable for the estimation of carbon in iron or steel. The following solutions are required:—1. A saturated solution of copper sulphate. 2. A solution of 100 grams of chromic acid in 100 c.c. of water. 3. A saturated solution of chromic acid in sulphuric acid of sp. gr. 1·65. 4. A similar solution in acid of sp. gr. 1·71. 5. Sulphuric acid of sp. gr. 1·1. 6. Commercial hydrogen peroxide. The process is carried out as follows:—0·5 gram of the sample (or a larger quantity if the sample is poor in carbon) is put into the flask and covered with 5 c.c. (or more in proportion) of the copper solution, which is allowed to act from 1 to 6 hours. Experiments made in the hope of accelerating the action by application of heat were unsuccessful. The mixture is now treated with the solution of chromic acid, 10 c.c. for every gram of the sample, then with the sulphuric acid of sp. gr. 1·65, of which 135 c.c. is used for 0·5 gram of sample, but only 130 c.c. for 1 or 2 grams. If more than 2 grams has been weighed out, from 75 to 70 c.c. of the sulphuric acid of sp. gr. 1·71 is used instead. Finally, sulphuric acid of sp. gr. 1·1 is

added; 30 c.c. for 0.5 gram of the sample, 25 c.c. for 1 gram, and 5 c.c. only for 2, 3, and 5 grams. Gentle heat is applied, when the carbon is rapidly oxidised to carbonic anhydride, which escapes into the measuring tube. To expel the last traces, from 1 to 2 c.c. of the hydrogen peroxide is introduced into the flask. This, when it comes in contact with the chromic acid, evolves oxygen, which sweeps out any carbonic anhydride. The mixed gases are measured as described in the previous paper, the carbonic anhydride is absorbed by aqueous soda, and so found by difference.

The test analyses are very satisfactory. It will be easily understood that the apparatus may be successfully employed for the estimation of free and combined carbonic acid in mineral waters.

L. DE K.

Estimation of Potassium as Perchlorate. By W. WENSE (*Zeit. angew. Chem.*, 1891, 691—693).—Owing to the high price of platinum chloride, other precipitants for potassium have been lately attracting attention, and more particularly perchloric acid. As, however, potassium perchlorate is decidedly soluble even in alcohol, its quantitative isolation is very difficult, but the author has vastly improved the method.

The commercial potash salts are freed from sulphates by the cautious addition of barium chloride, and the filtrate is then evaporated on the water-bath with a slight excess of perchloric acid until no more acid fumes escape. The residue is powdered and extracted with 96 per cent. (commercial absolute) alcohol, to which 2 per 1000 perchloric acid has been added, in which mixture the potassium perchlorate is all but insoluble. The insoluble mass is collected on a weighed filter (dried at 120°), and, finally, slightly washed with pure alcohol to remove the traces of free acid. After drying at 120°, the perchlorate may be weighed.

Perchloric acid may be conveniently prepared as follows:—1 part of potassium perchlorate is distilled in a strong retort with 2 parts of 90 per cent. sulphuric acid in a vacuum. The distillate is diluted, boiled, and freed from sulphate by cautious addition of barium chloride. After evaporating off any free hydrochloric acid, the liquid is again subjected to distillation. The author's test analyses are satisfactory.

L. DE K.

Estimation of Potassium. By F. JEAN and TRILLAT (*Bull. Soc. Chim.* [3], 7, 228).—The platinochloride, having been precipitated and purified in the usual way, is dissolved in water, and the solution, made alkaline with soda, is warmed and reduced by the addition of a few drops of aqueous formaldehyde; it should be stirred with a glass rod to prevent the platinum adhering to the vessel. The metal is then collected in the usual way.

JN. W.

Separation of Magnesium Chloride from the Chlorides of Sodium and Potassium. By R. B. RIGGS (*Amer. J. Sci.*, 44, 103—109).—Gooch (*Amer. Chem. J.*, 14, 33) has shown that both potassium and sodium chlorides are insoluble in anhydrous amyl alcohol, and may in this way be separated from the soluble lithium chloride.

He also called attention to the solubility of anhydrous magnesium chloride. The author found, however, a great difficulty in dehydrating this chloride without decomposition, but succeeded at last by adding to the amyl alcohol a few drops of benzyl chloride. This addition is, however, unnecessary when the mixed chlorides are treated as follows:—They are dissolved in as little water as possible and a few drops of hydrochloric acid added. 30 to 40 c.c. of amyl alcohol is then added and the water boiled off; the boiling is continued until the volume of the liquid is reduced to about 10 c.c. In filtering it is of great advantage to use a perforated crucible and an asbestos felt, and to filter under pressure. In case the total chlorides exceed 0.2 gram, the residue must be redissolved in a few drops of acid, and once more boiled with amyl alcohol; the filtrate is transferred to a weighed platinum dish and evaporated. Water is added before all the alcohol has been expelled, and the evaporation continued. Finally a slight excess of sulphuric acid is added; the residue is gently ignited, and weighed as MgSO_4 . L. DE K.

Detection of Strontium in presence of Calcium. By P. E. BROWNING (*Amer. J. Sci.*, **43**, 386—388).—The author (*Abstr.*, 1892, 915) has shown that calcium may be quantitatively separated from strontium by dissolving the mixed nitrates in a few drops of water and boiling with amyl alcohol. When the process is applied qualitatively, it will be found that, even in the absence of strontium, a slight deposit will form on the bottom of the test tube in which the boiling takes place. If this precipitate, after being washed with amyl alcohol, is redissolved in a drop of dilute nitric acid and again boiled with the amyl alcohol, it separates out wholly or partially. The author thinks that the deposit consists of the calcium salt of an organic acid formed by the action of the nitric acid on the fusel oil.

If, however, the deposit is first gently ignited before dissolving it in the nitric acid, it will completely dissolve in the amyl alcohol, and with care very minute proportions of strontium may be detected in presence of calcium. L. DE K.

Estimation of Barium in the presence of Calcium and Magnesium. By F. W. MAR (*Amer. J. Sci.*, **43**, 521—525).—It is a well-known fact that barium chloride is practically insoluble in strong hydrochloric acid, but the author has found that in order to make this a quantitative means of separation, some ether should be mixed with the acid. To utilise the process for the separation of barium from calcium, or magnesium, about 1 gram of the mixed chlorides must be dissolved in the smallest possible quantity of boiling water and precipitated by 25 c.c. of fuming hydrochloric acid. After cooling, 5 c.c. of pure ether is added. The acid should be added very gradually, so as to get the barium chloride in a coarse crystalline condition, when it is less liable to include foreign matter. After standing a few minutes, the precipitate is filtered into a Gooch's crucible, washed with hydrochloric acid containing 10 per cent. of ether, dried at 150—200°, and weighed as BaCl_2 .

The process, as shown by the test analyses, is accurate and rapid.

The fumes of the strong acid cause no inconvenience if the filtration is performed in front of a good flue. L. DE K.

Assay of Aluminium and some of its Alloys. By F. REGELSBERGER (*Zeit. angew. Chem.*, 1891, 442—446 ; 473—478).—*Estimation of Silicon in Aluminium*—The short process communicated by the author some time ago gives results which can never be scientifically correct, as some of the silicon escapes as hydride. Moreover, it does not distinguish between the two varieties of silicon. The new process is as follows:—4 grams of the cut up metal is dissolved, with the usual precautions, in a mixture of 30 c.c. of nitric acid, sp. gr. 1.35, and 70 c.c. of hydrochloric acid, sp. gr. 1.16. Whilst boiling, 30 c.c. of sulphuric acid is added and the evaporation continued until no more nitric fumes escape. About 200 c.c. of water is now carefully added and the insoluble matter is collected, washed and ignited in a platinum crucible. The product is crude silicic acid, which is weighed. It is then evaporated with hydrofluoric acid; the loss represents the silica. The residue is now again evaporated with hydrofluoric acid, but this time with the addition of nitric acid. The loss in weight represents the silicon. The red residue consists of a little ferric oxide.

Estimation of Aluminium in Ferro-aluminium.—5 grams of the alloy is dissolved in dilute sulphuric acid and heated until sulphuric fumes escape. The residue is then diluted with water to 300 c.c. 100 c.c. of the filtrate is reduced by boiling with iron wire or sodium hydrogen sulphite, then nearly neutralised with aqueous soda and poured into a boiling solution of 10 grams of potassium hydroxide in 50 c.c. of water mixed with 8 grams of potassium cyanide in 40 c.c. of water. The liquid is finally made up to 500 c.c. and 300 c.c. (= 1 gram metal) of the filtrate is boiled in a large porcelain dish with 15 grams of ammonium nitrate. The precipitate is thoroughly washed (best by means of a filter pump) and finally weighed as Al_2O_3 . It may be further tested as to its absolute purity.

Assay of Aluminium-copper and Aluminium-zinc-copper.—(1.) *Estimation of silicon*—5 grams of the alloy is dissolved in nitrohydrochloric acid, the solution evaporated to dryness, and the residue dissolved in dilute hydrochloric acid. Should the insoluble matter not be pure white, it must be fused with sodium potassium carbonate and the silica recovered from the melt as usual. The acid filtrate is added to the main filtrate. If the alloy is suspected to contain tin or lead, it is dissolved in nitric acid and evaporated with sulphuric acid. The insoluble matter is fused with the alkali carbonate, and then treated with nitric acid, when a mixture of silica and tin oxide will be obtained, in which the former may be estimated by evaporation with hydrofluoric acid. The lead will be found in the (nitric) acid filtrate. (2.) *Iron and aluminium*—If zinc is absent, an aliquot part of the filtrate is boiled with sodium thiosulphate to precipitate the copper as sulphide. The filtrate when poured into boiling potassium hydroxide yields a precipitate of ferrous oxide whilst the alumina dissolves, and may be recovered as usual. The iron precipitate may be obtained pure by redissolving it in nitrohydrochloric acid and reprecipitating with ammonia. (3.) If zinc is

present, the mixed iron and aluminium is first precipitated by means of ammonium acetate. In the filtrate, the zinc may be very conveniently estimated volumetrically by the ferrocyanide process in the absence of manganese. (4.) The copper is best estimated by electrolysis. 3 to 5 grams of the sample is dissolved in nitric acid and evaporated, with addition of sulphuric acid, to a syrupy consistence. The mass is then dissolved in water, filtered, and made up to a definite bulk from which an aliquot part is taken for the electrolytic estimation. (5.) Manganese, if present, will be found in the iron precipitate (2), and may be recovered from it in the usual manner.

L. DE K.

Estimation of Aluminium in Steel, Bronze, &c. By W. SCHÖNEIS (*Chem. Centr.*, 1892, ii, 132; from *Stahl u. Eisen*, 12, 527).—5—10 grams of steel turnings are dissolved in nitric acid (sp. gr. 1.2) in a large platinum dish, the solution evaporated to dryness, and the residue cautiously heated and finally ignited until all oxides of nitrogen are expelled. The residue is finely powdered in an agate mortar and fused in a silver dish with solid potash free from aluminium. The cooled mass is treated with hot water, filtered, and washed, and the aluminium in the filtrate precipitated by the addition of hydrochloric acid and ammonia. In the case of basic Martin steel, the alumina is pure; in the case of acid Martin steel, crucible steel, and ferro-aluminium, it contains silica, and must be treated with hydrofluoric acid.

C. F. B.

Separation of Iron, Aluminium, and Chromium. By C. MARCHAL and J. WIERNIK (*Zeit. angew. Chem.*, 1891, 511—513).—The two processes mostly used are the one introduced by Wöhler, who mixes the solution containing the three metals with potassium or sodium hydroxide in excess and then passes chlorine through the liquid until all the chromium has passed into the state of chromate, or the method proposed by Gibbs, who nearly neutralises the solution with sodium carbonate, adds excess of sodium acetate, and then oxidises by means of chlorine or bromine.

As, however, both processes fail, even qualitatively, if the amount of chromium is very small, the authors have searched for another oxidiser and found an excellent one in the shape of freshly precipitated manganese dioxide. To ensure success, the analysis must be carried out as follows:—The metals are, if possible, converted into sulphates or else into chlorides, and the solution is, as far as practicable, neutralised with sodium carbonate. Freshly-precipitated, well-washed manganese dioxide, prepared by mixing manganous sulphate (1 mol.) with potassium permanganate (1 mol.), is now gradually added, and the mixture boiled for about 10 minutes, which is generally sufficiently long to precipitate all the iron. The filtrate contains all the alumina and all the chromium as chromate, besides a little manganese, whilst the precipitate consists of ferric hydroxide and undissolved manganese dioxide.

To estimate the iron, the precipitate is dissolved in hydrochloric acid and boiled with sodium acetate. To free the iron precipitate completely from manganese, it must be redissolved in hydrochloric

acid and reprecipitated with ammonia. The filtrate is boiled and mixed with a little ammonia, which precipitates the alumina and also any manganese. The precipitate is then dissolved in hydrochloric acid, and treated with sodium acetate like the iron precipitate. The alkaline chromate is finally reduced as usual, and then precipitated with ammonia. The test analyses made on rather small quantities of a mixture of ferric, aluminium, and chromic oxides are fairly satisfactory.

L. DE K.

Colorimetric Estimation of Iron. By J. RIBAN (*Bull. Soc. Chim.*, [3], 7, 199—200; Abstr., 1892, 240, 1132).—The author maintains that Lapicque's thiocyanate method can only be carried out under very special conditions, owing partly to the dissociation of ferric thiocyanate in dilute solution, and partly to the impossibility of procuring standard coloured glasses of uniform colour.

JN. W.

Estimation of Vanadium in Ores. By L. L'HÔTE (*Ann. Chim. Phys.* [6], 22, 409—412).—See this vol., ii, 17.

Estimation of Cyanogen in Spent Materials from Gas Purifiers and in Illuminating Gas. By H. DREHSCHMIDT (*Chem. Centr.*, 1892, i, 1006—1008; from *J. Gasbeleucht. Wasserversorg.*, 35, 221—226, 268—270).—*Estimation of Cyanogen in Spent Materials.*—A mixture of 10 grams of the spent material, about 150 c.c. of water, 1 gram of ammonium sulphate, and 15 grams of mercuric oxide are placed in a 500 c.c. flask and boiled for 15 minutes. After cooling, 0.5—1 c.c. of a saturated solution of mercurous nitrate is run in, and then ammonia is added until no further precipitate is formed. The flask is filled up to the mark, and an additional 8 c.c. of water, corresponding with the volume of the solid matter present, is added. After shaking thoroughly, the liquid is passed through a dry filter, and 200 c.c. of the filtrate (corresponding with 4 grams of the material) is placed in a 400 c.c. flask and treated with 7 grams of zinc dust and at least 6 c.c. of ammonia solution (sp. gr. 0.91). The mixture is shaken several times, 2 c.c. of 30 per cent. potassium hydroxide solution is added, and the liquid is made up to 401 c.c. and filtered through a dry filter. 100 c.c. of the filtrate (corresponding with 1 gram of the substance) is added to excess of N/10 silver nitrate solution contained in a 400 c.c. flask, the liquid is acidified with nitric acid, the flask filled up to the mark, and the solution again filtered. Finally, 200 c.c. of this last filtrate is titrated by Volhard's method with N/20 ammonium thiocyanate. The required quantity of this solution directly corresponds with the excess of silver, and by subtracting it from the total volume of silver solution employed, the amount of silver corresponding with cyanogen is obtained [1 c.c. 1/10 normal solution of silver nitrate = 0.002598 gram cyanogen (0.2598 per cent.) = 0.004771 gram $\text{Fe}_2\text{Cy}_{13}$ (0.4771 per cent.).]

Under some conditions, for example, when compounds containing chlorine are present, mercurous nitrate cannot be satisfactorily employed, and the author then uses potassium iodide in its place. The titration is then complete as soon as the turbidity caused by silver

iodide is persistent, after repeated additions of 5—10 c.c. of 30 per cent. potassium hydroxide solution.

Estimation of Cyanogen and Hydrocyanic Acid in Illuminating Gas.—Potassium hydroxide alone is not a good absorbent of hydrocyanic acid, but when it contains ferrous hydroxide in suspension the absorption is complete. The author employs an absorption apparatus consisting of a wide cylinder fitted with a stopper with two holes. Through one of these the gas enters and passes to a small glass bell, from which it escapes through the absorbent liquid by a number of perforations on the upper side. To estimate the cyanogen, the gas is passed through two absorption cylinders, the first containing 15 c.c. of ferrous sulphate solution (1 : 10) and 15 c.c. of potassium hydroxide solution (1 : 3), and the second, 5 c.c. of ferrous sulphate solution, 5 c.c. of potassium hydroxide solution, and 20 c.c. of water. Under ordinary conditions, 100 litres of gas is employed, and it is allowed to pass through the apparatus at the rate of 60—80 litres per hour. The contents of the absorption-cylinders are made up to 250 c.c. and filtered. 200 c.c. of the filtrate is placed in a 300 c.c. flask, neutralised with an equivalent quantity of sulphuric acid, mixed with ammonium sulphate (2 grams) and mercuric oxide (15 grams), and boiled for 15 minutes. When cold, the bulk is made up to 301·3 c.c., the solution is filtered, and 250 c.c. of the filtrate is placed in a 300 c.c. flask with 6—10 c.c. of ammonia (sp. gr. 0·91) and 7 grams of zinc dust. After shaking thoroughly, 2 c.c. of potassium hydroxide is added, the solution is made up to 301 c.c., again shaken, and passed through a dry double filter paper. To 200 c.c. of the filtrate 30 c.c. of potassium iodide solution is added, and the resulting solution is titrated with N/20 silver solution, in the manner described above. If n is the silver required, the expression $2\cdot598\ n\ 9/4$ gram gives the weight of cyanogen in 100 c.c. of the gas.

G. T. M.

Estimation of Glycerol by Benedikt and Zsigmondy's Process. By C. MANGOLD (*Zeit. angew. Chem.*, 1891, 400—401).—The author has modified the process, and operates as follows:—0·4 gram of the sample is dissolved in a litre flask, in 300 c.c. of water containing 10 grams of potassium hydroxide, 55 c.c. of a 5 per cent. solution of potassium permanganate is slowly added, and the mixture allowed to remain for about half an hour. Solution of hydrogen peroxide is then added until the manganese is precipitated and the supernatant liquid looks quite colourless, after which water is added up to the mark, the whole thoroughly mixed, and 500 c.c. filtered through a dry filter. After boiling the filtrate in a flask for half an hour to destroy the excess of hydrogen peroxide, the liquid, which contains oxalic acid derived from the oxidation of the glycerol, is cooled to 60°, acidified with sulphuric acid, and titrated with permanganate. The test analyses are satisfactory. The presence of butyric acid does not interfere.

L. DE K.

Estimation of Inorganic Constituents in Sugars. By ALBERTI and HEMPEL (*Zeit. angew. Chem.*, 1891, 486—492).—The conventional sulphuric acid process, although convenient and safe, is really very

untrustworthy, particularly if the sample contains any sandy matter. The authors, who communicate the results of more than 200 experiments, now recommend the following process:—About 6 or 7 grams of coarsely powdered quartz is ignited in a 35 c.c. platinum dish, and after cooling, the whole is weighed. 5 grams of the sugar is now introduced, and after this is well mixed with the sand by means of a thin platinum wire, the dish is placed in a platinum muffle and ignited with a full flame. The sugar burns quietly without frothing. After half an hour, sometimes longer, the operation is finished, and the ash may be weighed. If dealing with molasses, about 3 grams of the sample is a convenient quantity to work on. The ash is free from carbonic acid, and as chlorides and sulphates are not decomposed by the heated silica, the true mineral matter of the sugar is obtained.

L. DE K.

Estimation of Sugar and Tannin in Wine. J. H. VOGEL (*Zeit. angew. Chem.*, 1891, 449).—The author (Abstr., 1891, 1557) states that by adopting Bornträger's plan, the decolorisation of very deeply coloured wines may be effected by a comparatively small quantity of basic lead acetate without interfering with the accurate estimation of the sugar; but he still uses, by preference, animal charcoal, which not only removes the colouring matter, but also any tannin.

L. DE K.

Estimation of Pentosans and Pentoses in Vegetables. By E. R. FLINT and B. TOLLENS (*Ber.*, 25, 2912—2917).—Continuing their work on this subject (Abstr., 1892, 388), the authors have confirmed their previous results. They recommend the gravimetric estimation of the furfuraldehyde hydrazone as the most exact and convenient. Care must be taken that the quantity of sodium chloride in the 500 c.c. of neutralised distillate is always 81.5 grams (that is, the quantity of sodium chloride produced by the neutralisation of 400 c.c. of distillate containing 12 per cent. of hydrogen chloride). If the distillate is less than 400 c.c., 10.2 grams of sodium chloride is added for every 50 c.c. deficiency of distillate before neutralisation, addition of phenylhydrazine, and making up to 500 c.c. The following factors were determined:—

1. Arabinose = hydrazone \times 1.229 + 0.0177.
2. Xylose = hydrazone \times 1.031 - 0.001.
3. Pentose (average, if kind unknown) = hydrazone \times 1.13 + 0.0083.
4. Furfuraldehyde = hydrazone \times 0.516 + 0.0254.
5. Pentosan (araban or xylan) = pentose \times 0.88.

The presence of starch or cane sugar interferes to some extent with the determination, causing rather too low numbers to be obtained. Cellulose does not appear to affect the results.

Günther's titration method (*loc. cit.*) gives rather too high results, owing to the levulinic acid, &c., which is usually present in the distillate also forming hydrazones. As those hydrazones are pretty soluble, they do not influence the gravimetric method.

The authors have determined the amounts of pentosans, &c., in a number of woods, gums, &c. L. T. T.

Estimation of Stachyose in the Tubers of *Stachys tuberifera*.

By A. v. PLANTA and E. SCHULZE (*Landw. Versuchs-Stat.*, 41, 123—129; compare Abstr., 1891, 1446).—It has been already shown that stachyose is by far the most prominent constituent of the sap of the tubers. The stachyose was first estimated with the polariscope; the washed and dried tubers were mashed, 250 grams quickly weighed, treated with lead acetate solution (20 c.c.) and alcohol (50 c.c.), and water added to make up to 800 c.c. When filtered, a portion was polarised in a 200 mm. tube. The results of this and a second experiment showed the percentage of stachyose to be 14.16 (14.2 and 14.13) in the fresh, and 73.07 per cent. in the dry tubers. A direct estimation in the expressed sap gave a percentage of 15.6. Attempts to determine the stachyose by treatment with hydrochloric acid and estimation of the glucose with Fehling's solution failed; acid of the strength required for inverting cane sugar was insufficient; with stronger acid, there is a danger of destroying a portion of the levulose formed.

The stachyose was next estimated as mucic acid after treatment with nitric acid. Weighed amounts of the powdered tubers were extracted with hot water, the extracts treated with slight excess of lead acetate, filtered, the filtrate treated with hydrogen sulphide, again filtered, and evaporated on the water-bath. The syrup was dissolved in nitric acid (sp. gr. 1.15), and evaporated at a gentle heat to about one-third of its bulk. 1 gram of stachyose (calculated from the polarimetric determination) required about 12 c.c. of nitric acid of the above sp. gr. The experiment was continued according to Tollens' method. The mean of the first two experiments was 63.3 per cent. of stachyose in the dry matter; the third experiment gave 61.6 per cent. That the results were lower than those obtained with the polariscope may be due to the presence of a second carbohydrate in the sap which is also dextrorotatory, but does not yield mucic acid when oxidised; or else the stachyose, when oxidised in presence of other substances, gives less mucic acid than when oxidised alone. It seems certain that it is not the first reason alone which caused the difference. The percentage obtained by polarisation is probably nearest the truth.

Besides stachyose, the tubers contain a second carbohydrate, which yields furfuraldehyde (1.98 per cent.) by de Chalmot and Tollens' method. It is concluded that the substance is a pentosan, that is, a carbohydrate which yields a pentose when treated with dilute acid. The amount in the dry tubers would be about 3.5 per cent. It is questionable whether it occurs in the sap. N. H. M.

Estimation of Acids in Beer. By PRIOR (*Chem. Centr.*, 1892, i, 767; from *Freie Verein. bayer. Vertreter. angew. Chem.*, 10, 22—34).—The presence of secondary and primary phosphates in beer offers a great impediment to the determination of the free acids contained in it. Results, more satisfactory than those given by processes previously

described, are obtained as follows:—50 c.c. of the beer is freed from carbonic anhydride, and mixed, first with 150 c.c. of alcohol, then with 300 c.c. of ether. After remaining for 12 hours, the liquid is filtered, the ether is distilled off, and the alcoholic residue made alkaline with a known volume of N/10 sodium hydroxide solution. The alcohol is then distilled off, an equivalent quantity of N/10 sulphuric acid added, and the volatile acids distilled in a current of steam. The residue, after the distillation, contains only the free, non-volatile organic acids, together with a small quantity of acid phosphates and some neutral extractive matter. It is carefully titrated with alkali, and the neutral solution mixed with clean sea-sand and evaporated to dryness. The residue is treated with a quantity of N/10 sulphuric acid equivalent to the alkali recently added, heated on a water-bath and, after cooling, rinsed into a flask with 50 c.c. of alcohol and then mixed with 100 c.c. of ether. This treatment completely separates the organic acids from the phosphates. After evaporation of the alcohol and ether at the lowest possible temperature, the extract is titrated; whilst the sandy residue is also titrated in aqueous solution; the precipitate obtained on first adding alcohol and ether to the beer being treated in a similar way, so that the sum of both titrations gives an expression for the primary phosphates contained in the beer. The remainder of the acid phosphate, which goes into solution, is very small in comparison with the total quantity of phosphates.

Experiments show that it is most difficult to separate the acetic acid contained in beer in a satisfactory way. In order to estimate lactic acid and succinic acid in a mixed aqueous solution, they were carefully titrated with calcium hydroxide solution, evaporated to dryness, and digested with 90—98 per cent. alcohol. After 24 hours, the calcium succinate was collected, ignited and weighed as calcium oxide, and the amount of lactic acid present calculated by difference. No perfect method of estimating these acids in beer has yet been suggested.

G. T. M.

Estimation of Succinic Acid. By A. RAU (*Chem. Centr.*, 1892, ii, 155—157; from *Revue Hygiène*, 14, 225—242).—See this vol., i, 11.

Estimation of Citric Acid in Wine. By A. KLINGER and A. BUJARD (*Zeit. angew. Chem.*, 1891, 514—515).—The authors recommend the following process, which they use in preference to the one adopted by Nessler and Barth, as there is less danger of mistaking calcium malate for citrate. 250 c.c. of the wine is evaporated to about 80 c.c., acidified with acetic acid, and after adding some potassium acetate, mixed with 160 c.c. of strong alcohol. After 24 hours, the liquid is filtered, and the residue rinsed with a few c.c. of dilute spirit to redissolve traces of potassium citrate. The filtrate is then at once precipitated with basic lead acetate; the precipitate is collected on a filter, washed with dilute alcohol, and then decomposed by hydrogen sulphide in the usual manner.

The filtrate from the lead sulphide is concentrated and made slightly alkaline with milk of lime. After a few hours, the liquid is

filtered from any traces of calcium tartrate and phosphate. The filtrate is acidified with acetic acid and evaporated to dryness. The residue is dissolved in water with addition of a little hydrochloric acid, a little ammonium chloride is added, and after adding excess of ammonia, the whole is continually boiled. Any precipitate can now only be calcium citrate, as the malate is soluble in a boiling solution of ammonium chloride.

L. DE K.

Estimation of Milk Fat with Demichel's Lactobutyrometer.

By L. GRAFFENBERGER (*Landw. Versuchs-Stat.*, 41, 43—54). Demichel's lactobutyrometer is constructed on the same principle as Marchand's, but differs from it in having a narrow tube for reading off the amount of fat, the fat being raised into this tube by the addition of water through a second tube (compare *Milchzeit.*, No. 23, 1891). The tube is graduated from 12.6 to 70. The method is as follows:—10 c.c. of milk is poured from a pipette into the apparatus, 2 drops of alkali solution, 10 c.c. of ether, and 10 c.c. of alcohol added, and the whole violently shaken. The apparatus is placed in water at 40° for 10 minutes, and then so much water added that the lower surface of the fat layer corresponds with the 12.6 mark; the amount of fat is then read off, the numbers showing the amount, in grams, in 1 litre of milk. The addition of water has to be made with great care, otherwise a part of the fat will again mix with the water. It is also very difficult in adding water to get the lower surface of the fat to correspond with the mark, and it would be preferable, instead of having the degrees marked on the glass, to have them on a movable metallic sheath, which could always be so placed as to correspond with the layer of fat. With regard to the method itself, it was found that aqueous potash (sp. gr. = 1.27) was of a suitable strength. The alcohol should be 91—92 per cent.; 40° is a better temperature for the separation than 20° (recommended by Tollens and Schmidt), but the amount of fat should be read off at 20°, after an interval of 30 minutes, as during the cooling there is a further separation of fat.

A number of results obtained by this method are given, together with results obtained by Soxhlet's method. Most of the results are very near the truth, but single estimations have little value. Averages of several results are, however, to be trusted; the averages obtained by the author differed only 0.1—0.2 per cent. from the Soxhlet results. By excluding such results as differ most from the others, averages were obtained which differed only 0.02—0.06 per cent. from Soxhlet's. The results were obtained after ascertaining the value of the calibration, calculating the divisions to $\frac{1}{10}$ c.c., and then the amount of fat by means of Schmidt and Tollens' table. It would be better to give up the empirical division on the Demichel apparatus, and to employ a scale showing $\frac{1}{10}$ c.c.

Although not at all equal to Soxhlet's, as regards accuracy, the Demichel apparatus is worthy of consideration, owing to the ease with which it is employed and its cheapness; but, on no account should the apparatus, as now made, be used without a previous comparison of the results it gives with those obtained either by a Soxhlet apparatus or gravimetrically.

N. H. M.

Melting Point and Composition of Butter from Cows variously fed. By A. MAYER (*Landw. Versuchs-Stat.*, **41**, 15—35).—See this vol., p. 28.

Testing Linseed Oil Varnish. By W. FAHRION (*Zeit. angew. Chem.*, 1891, 540).—It is sometimes useful to know the state of oxidation of a linseed oil varnish. The process to be described is based on the fact, first noticed by the author, that the unsaturated fatty acids, on oxidation, yield compounds which are insoluble in light petroleum, and may in this manner be separated from the saturated fatty acids or their oxy-products.

The analysis is carried out as follows:—About 3 to 5 grams of the varnish is weighed out and saponified by means of 15 to 25 c.c. of an 8 per cent. alcoholic potash. After the spirit has been completely expelled, the soap is dissolved in 50—70 c.c. of hot water, and then transferred to a half-litre separating funnel. After decomposing the soap by means of hydrochloric acid, and subsequent cooling, the whole is shaken with 100 c.c. of light petroleum, and allowed to remain for about an hour. The aqueous liquid is now completely drawn off, and if any oxy-acids are present these will be found adhering to the sides of the funnel. The clear petroleum layer is carefully drawn off, and, after washing two or three times with light petroleum, the oxy-acids are dissolved in a little hot alcohol, and transferred to a weighed dish. After expelling the alcohol, the residue is finally dried for an hour at 100—105°.

The amount of oxy-acids found by the author in various samples of linseed oil varnish varied from 0.6 to 31.6 per cent. L. DE K.

Estimation of Aniline, Methylaniline, and Dimethylaniline. By F. REVERDIN and C. DE LA HARPE (*Bull. Soc. Chim.* [3], **7**, 211—212).—See this vol., i, 24.

Analysis of Linseed Cake. By A. HASELHOFF (*Landw. Versuchs-Stat.*, **41**, 54—72; and by F. J. VAN PESCH, *ibid.*, 73—93).—See this vol., ii, pp. 39, 40).

Detection of Cochineal in Sausages. By A. KLINGER and A. BUJARD (*Zeit. angew. Chem.*, 1891, 515—516).—20 grams of the cut up sausage is heated in a water-bath with a mixture of equal parts of water and glycerol. If any carmine is present, the liquid gets decidedly reddish, but in its absence only a slight yellow colour is noticed. The solution is filtered, and, if necessary, heated with another 20 grams of the sample. The clear liquid, which is, of course, free from fatty matter, is then examined in the spectroscope, when any carmine will be readily recognised by its characteristic absorption bands. Or the colouring matter may be precipitated as a lake, and this, after washing, may be dissolved in a little tartaric acid. In this way a more concentrated solution of the colouring matter is obtained, and the spectroscopic test is consequently more satisfactory.

L. DE K.

General and Physical Chemistry.

Molecular Refractive Power of Organic Compounds for Infinite Wave-length. By H. LANDOLT and H. JAHN (*Zeit. physikal. Chem.*, 10, 289—320).—From measurements for electrical waves of great wave-length, it has been shown that Maxwell's relation, $n^2 = k$, between the index of refraction and the dielectric constant is true for a considerable number of solid and liquid substances. The authors have determined this constant for several series of organic substances and have introduced it into Lorentz's formula, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$, in order to determine the specific refraction equivalents for infinite wave-length. The accompanying table gives the values of \sqrt{k} and of A, the first constant of Cauchy's dispersion formula, which should also be equal to n for substances of normal dispersion.

	\sqrt{k} .	A.
Hexane	1.3608	1.3683
Octane	1.3899	1.3902
Decane	1.4015	1.4001
 Amylene	 1.4836	 1.3750
Octylene	1.4758	1.4030
Decylene	1.4764	1.4246
 Benzene	 1.4816	 1.4777
Toluene	1.5410	1.4743
Ortho-xylene	1.6101	1.4838
Metaxylene	1.5322	1.4755
Paraxylene	1.4942	1.4744
Ethylbenzene	1.5543	1.4756
Propylbenzene	1.5333	1.4703
Isopropylbenzene	1.5417	1.4718
Mesitylene	1.5157	1.4741
Pseudocumene	1.5462	1.4835
Isobutylbenzene	1.5309	1.4742
Cymene	1.4948	1.4712
 Methyl alcohol	 5.496	 1.3216
Ethyl " 	5.248	1.3527
Propyl " 	4.629	1.3762
Isobutyl " 	4.287	1.3865
Isoamyl " 	4.041	1.3978

From the table it appears that only the paraffins have normal dispersion, and that the alcohols in especial are very anomalous. The following values of k were also determined.

Ethylene chloride.....	11.315
Ethylidene chloride.....	10.861
Methyl acetate.....	8.0165
Ethyl acetate.....	6.7381
Propyl acetate.....	6.639
Isobutyl acetate.....	5.6808
Amyl acetate.....	5.0695
Ethyl formate.....	9.102
Propyl formate.....	9.0163
Isobutyl formate.....	7.2801

The temperature of experiment ranged from 0° to 23°. J. W.

Infra-Red Emission Spectrum of the Alkalis. By B. W. SNOW (*Ann. Phys. Chem.* [2], **47**, 208—251).—The infra-red spectrum of the electric arc into which salts of the alkalis were introduced was investigated by means of a sensitive bolometer, constructed of two fine Wollaston platinum wires, one of which was flattened and exposed to the different parts of the spectrum in succession. As the exposed surface of the bolometer was very small ($1\frac{1}{2}$ sq. mm.) a very sensitive galvanometer had to be employed, details of the construction of which are given in the paper. A flint glass prism of strong dispersion was used to produce the spectrum. An investigation of the spectrum of the electric arc itself showed that the maximum of energy (measured by the deflection of the galvanometer) lay further out towards the violet than the Fraunhofer lines H_1 and H_2 , namely, from $\lambda = 0.385\mu$ to $\lambda = 0.388\mu$. In order to get the alkali salts (chlorides) introduced into the arc, both the carbon poles, 8 mm. in diameter, were drilled out axially and the boring was then filled with the salt under examination. The diameter of the hole in the positive (lower) carbon was 3 mm., in the negative carbon 1.5 mm. With this arrangement, the carbon spectrum is totally destroyed and the pure metal spectrum takes its place.

The results obtained are exhibited in tabular and in curve form. All the alkali metals were investigated. In the case of lithium and sodium, the wave-lengths of the lines observed agree well with those calculated by Kayser and Runge. With the other metals, there are considerable discrepancies. J. W.

Electromotive Force of Oxidation Cells. By W. D. BANCROFT (*Zeit. physikal. Chem.*, **10**, 387—409).—Two test tubes, one containing an oxidising solution, the other a reducing solution, had their contents electrolytically connected with each other by means of side-tubes and an inverted siphon filled with a solution of sodium chloride. Electrodes of platinum, cut from the same piece of foil, were immersed in the liquids and the electromotive force between them measured by means of the galvanometer, a Latimer-Clark cell being used as standard. In all, 17 oxidising solutions and 24 reducing solutions were examined. The usual concentration was $\frac{1}{2}$ normal, and the temperature of experiment varied from 16° to 18°.

The results arrived at by the author are as follows. The electro-

motive force of oxidation cells is an additive property, that is, it is equal to the sum of two terms, one depending on the nature of the oxidising agent and the other on the nature of the reducing agent. It is independent of the nature of the electrodes, if these are not attacked, and is also (within wide limits) independent of the concentration of the solutions. The nature of the solution which effects the electrolytic connection is without influence on the electromotive force. A free acid is a stronger oxidising agent than its alkaline salts; the converse holds true for reducing agents. Under these restrictions, the electromotive force is, in general, independent of the nature of the indifferent ions. The electrodes are not always non-polarisable, as theory requires; but the variations may usually be attributed to secondary influences. J. W.

Electrolytic Conductivity and Dissociation. By J. BROWN (*Phil. Mag.* [5], 33, 82—89).—The electrolytic dissociation theory and Arrhenius and Claisen's theory of electrolytic conductivity from which it is derived are adversely criticised by the author, in the sense that neither is requisite to explain known facts. J. W.

Specific Heat of the Atoms and their Mechanical Constitution. By G. HINRICHS (*Compt. rend.*, 115, 239—242).—If m is the mass of an elementary atom and v its velocity of maximum vibration, and M the mass of any compound radicle composed of n atoms of m and with a velocity, \bar{V} , round its centre of gravity, $2E' = \Sigma mv^2 + M\bar{V}^2$, where E' is the total energy of vibration. But also $M\bar{V}^2 = 2kT$ and $mv^2 = 2\rho kT$, where k and ρ are constants and T the absolute temperature, so that $E' = k(1 + \rho n)T$. The specific heat due to the vibrations of the atoms will then be $s' = \frac{dE'}{dT} = k(1 + \rho n)$. This formula shows that the specific heat of the compound radicle increases with the number n of the elementary atoms which it contains. For elementary substances, the atomic heat will be independent of n , and therefore constant. In this case ρ will be nothing, or the independent velocity of vibration of the particles composing m will be nothing. That is to say, in compound substances or radicles, the constituent elemental atoms possess their own peculiar motion of vibration, but in elementary substances the constituent atoms are incapable of individual vibration. It is therefore not surprising that hitherto all efforts at decomposing elementary substances have failed. H. C.

Heat of Combustion of Organic Compounds. By F. STOHMANN (*Zeit. physikal. Chem.*, 10, 410—424).—The author continues the tabulation of the heats of combustion of organic compounds in the manner previously described (*Abstr.*, 1891, 251). Data for nearly 300 compounds are given, the following classes being represented:—hydrocarbons, alcohols, carbohydrates, phenols, camphor-derivatives, phenol ethers, aldehydes, acids, anhydrides, lactones, lactic acids, ketones, ethereal salts, amides, amido-acids, amines, azo-compounds, nitro-compounds, proteids, chloro-compounds, and hydrochlorides.

J. W.

Constitution of Phosphoric Acid and the Thermal Value of its three Acid Functions. By DE FORCRAND (*Compt. rend.*, 115, 610—613).—The heat of dissolution of anhydrous mono-sodium phosphate is -0.13 Cal. at 20° , and combining this result with the results of previous investigators of the thermal behaviour of phosphoric acid, it follows that:—

H_3PO_4 sol. + Na sol. = H gas + NaH_2PO_4 sol.	develops + 60.60 Cal.
NaH_2PO_4 sol. + Na sol. = H gas + Na_2HPO_4 sol.	„ + 49.20 „
Na_2HPO_4 sol. + Na sol. = H gas + Na_3PO_4 sol.	„ + 38.33 „
H_3PO_4 sol. + Na_3 sol. = H_3 gas + Na_3PO_4 sol.	„ + 148.13 „

The total thermal value of the three acid functions of phosphoric acid is $+148.13$ Cal. and the mean value of each function is $+49.38$ Cal. The apparent value of the first function, however, is $+60.60$ Cal., and of the third only $+38.33$ Cal. These results agree with the supposition that phosphoric acid has the constitution $\text{PO}(\text{OH})_3$, and its molecule is symmetrical in the same manner as the molecule of sulphuric acid, glycol, or pyrogallol. The value of the first acid function is exaggerated by the occurrence of intramolecular combinations between the unsaturated acid functions, similar to those already observed by the author in the case of polyhydric alcohols and phenols, and the apparent value of the third acid function is lower, because of the absorption of energy required to break up these intramolecular combinations before the acid can be completely saturated.

C. H. B.

Temperature of Maximum Density of Aqueous Solutions. By L. DE COPPET (*Compt. rend.*, 115, 606—607).—Despretz, in 1839, formulated a law for the reduction of the point of maximum density of water which is similar to that of Blagden for the reduction of the freezing point, and states that the reduction of the temperature of maximum density below 4° is proportional to the weight of substance dissolved in 100 parts of water. The author is now able, as a result of his own observations, to bring the laws for the reduction of the maximum density into further accordance with those for the reduction of the freezing point, and to state that substances of similar composition, and in some cases of very different composition, have the same molecular reduction of the temperature of maximum density. This law obtains within the same limits to which the law of the reduction of the freezing point applies. Only one exception has, up to the present, been found, and this is in the case of solutions of ethyl alcohol and water, as mixtures of the two behave abnormally with respect to the reduction of the freezing point (see next abstract).

An interesting relation exists between the reduction of the freezing point C and that of the temperature of maximum density D . Substances generally may be divided into three groups according to the values of the ratio D/C . In the first group, at present comprising

potassium hydroxide, oxalic acid, the chlorides of sodium, potassium, and calcium, and potassium iodide, the value of this ratio is about 4. In the second group, containing sugar, and the carbonates and sulphates of the alkali metals, the value is from 7 to 8. In the third group, of which copper sulphate is as yet the only representative, the value is from 11 to 12. The three values for the ratio D/C are, therefore, as will be seen, themselves approximately in the proportion 1 : 2 : 3.

H. C.

Temperature of Maximum Density of Mixtures of Alcohol and Water. By L. DE COPPET (*Comp. rend.*, 115, 652—653).—In a former paper (preceding abstract), the author pointed out that solutions of alcohol in water do not obey the law which he has formulated for the reduction of the temperature of maximum density. The following table, compiled from his own observations and those of Despretz and Rossetti, illustrates the abnormal behaviour of alcohol in this respect:—

$M.$	$C.$	$D.$	$\frac{C}{M}$	$\frac{D}{M}$
0·09	0·00°	— 0·12°	0·000	—1·333
0·642	0·27	— 0·16	0·421	—0·249
1·346	0·54	— 0·29	0·401	—0·215
2·568	1·03	— 0·39	0·401	—0·152
3·943	1·57	— 0·02	0·398	—0·005
6·21	2·63	+ 0·83	0·424	+ 0·134
6·575	2·60	+ 1·15	0·395	+ 0·175
7·408	2·83	+ 1·75	0·382	+ 0·236
8·46	3·54	+ 2·18	0·418	+ 0·258
10·80	4·45	+ 4·19	0·412	+ 0·388
17·12	7·47	+ 12·48	0·436	+ 0·729

The first column contains the weights of alcohol in 100 grams of water, the second the reduction of the freezing point, the third the reduction of the temperature of maximum density, and the fourth and fifth the numbers in the second and third columns divided by those in the first. It will be seen that although the solutions obey Blagden's law with regard to the reduction of the freezing point, the reduction of the temperature of maximum density is not proportional to the quantity of alcohol present. Indeed, for dilute solutions, there is an actual rise instead of a fall in the temperature of maximum density.

H. C.

Density and Composition of Sulphuric Acid Solutions. By A. W. RÜCKER (*Phil. Mag.* [5], 33, 204—209; compare Abstr., 1892, 271—272).—This paper is a continuation of the discussion between the author and Pickering as to the use of the bent lath in detecting changes of curvature in curves representing experimental data. The author states his position with regard to the density curve for sulphuric acid at 18° as follows:—"Any peculiarity in a curve on which

argument is founded must be proved to be outside the error of experiment. No weight can be attached to a representation which is not unique in the sense that no other is compatible with the observations when all allowance is made for experimental error. Mr. Pickering's first solution (the four-break one) is not unique. He has himself offered another (one break), and I have contributed a third (no breaks). . . . Put briefly, the observations, accurate and numerous as they are, are not accurate enough, and not numerous enough, to decide whether the 18° density curve is, or is not, discontinuous between 47 per cent. and 80 per cent."

J. W.

Dissociation Measurements of Feebly Dissociated Acids. By J. E. TREVOR (*Zeit. physikal. Chem.*, 10, 321—353).—It has been shown by Arrhenius that the rate of inversion of sugar by acids is, *cæteris paribus*, proportional to the concentration of the hydrogen ions in the solution. This rate increases very rapidly with the temperature, so that at 100° it is possible to measure, by this means, the amount of hydrogen ions produced by the dissociation of a very feeble acid when other methods fail. The author has worked out the method for high temperatures, and gives a detailed description of the apparatus employed. The substances chiefly studied were the hydrogen sodium salts of the oxalic acid series.

From his observations, the author draws the following conclusions:—

The inversion constant, which corresponds with total inversion, is 17.92 at 100°.

The percentage increase of the inversion constant per degree rise of temperature is the same, or nearly the same, for all acids in a given range of temperature.

The electrolytic dissociation of organic and inorganic acids is, in general, almost independent of the temperature, at least between 25° and 100°.

The dissociation of hydrogen from the acid salts of the bibasic organic acids is relatively small, sinking as low as 0.03 per cent. for the higher members of the series at a dilution of 32, and seldom reaching 1 per cent. at a dilution of 256. The dissociation of these substances follows the same law in all cases, the degree of dissociation being nearly proportional to the dilution, instead of to the square root of the dilution as is the case for the acids themselves. When the acid salts are arranged in order of the amount of dissociation of hydrogen at a given dilution, this order is the same as that of the dissociation constants of the free acids themselves.

J. W.

Diffusion of Oxygen and Nitrogen in Water. By C. DUNCAN and F. HOPPE-SEYLER (*Zeit. physiol. Chem.*, 17, 147—164).—A tube was first emptied, then filled with boiled water. This was exposed to the action of the atmosphere for varying periods, and the gases absorbed pumped off and analysed. Daily observations on barometric pressure and temperature were made. The total amount of gas absorbed increased with the duration of the exposure; the daily increment in the amount absorbed, however, gradually diminishes.

The results are given in extensive tables for oxygen, nitrogen, and carbonic anhydride at different depths below the surface. From the results, the conclusion is drawn that in the great depths of the sea or lakes, animals, if they live, either require less oxygen, or that the gaseous exchange between the water and the atmosphere is carried out by other means than diffusion. (See this vol., ii, 81.)

W. D. H.

Van der Waals' Corresponding States. By S. YOUNG (*Phil. Mag.* [5], 33, 153—185).—In a series of tables and curves, the author gives the critical constants, corresponding temperatures and pressures, molecular volumes in corresponding states, and various ratios between these magnitudes, for different substances. Benzene, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, carbon tetrachloride, stannic chloride, ether, methyl alcohol, ethyl alcohol, propyl alcohol, and acetic acid form the material studied by the author.

Van der Waals' statement that, "if the absolute temperatures of various substances are proportional to their absolute critical temperatures, their vapour pressures will be proportional to their critical pressure," proves not to be true except in a very limited number of cases, and occasionally it is very wide of the mark. From this, it follows that in the comparison of molecular volumes, the ratios at corresponding pressures must differ from those at corresponding temperatures. The deviations of the molecular volumes of liquids are smaller than the deviations in any of the other cases, but still not within the limits of experimental error. The comparisons at corresponding pressures are somewhat better than at corresponding temperatures. In the case of the molecular volumes of saturated vapours at corresponding pressures, the deviations from constancy are within the limits of experimental error for ether and stannic chloride, and are relatively small for benzene and carbon tetrachloride.

When the alcohols, which differ widely from the other substances studied, are compared amongst themselves, the deviations are much smaller than before, but still far outside the error limit.

Double molecules of acetic acid probably exist even at the critical temperature.

The author gives details of the manner of determining the critical volumes of the various substances, and discusses some relations advanced by himself and by Guye.

J. W.

Method of Measuring Loss of Energy due to Chemical Union, &c. By G. GORE (*Phil. Mag.* [5], 33, 28—53; compare *Abstr.*, 1892, 257, 930).—The author measures the electromotive force of a voltaic couple consisting of platinum and of another metal (usually aluminium, tin, cadmium, zinc, or magnesium), immersed in two solutions separately, and then in the solution resulting on mixing the two. He gives the following sketch of his method:—Take a known quantity of an acid dissolved in a known weight of water, and measure the electromotive force *A* developed by a small couple of platinum and aluminium immersed in the solution. Take a chemically equivalent quantity of a base dissolved in the same

weight of water, and find the electromotive force B developed by the same element. Again, ascertain the electromotive force C in an equivalent solution of the salt resulting from the combination of the acid and base. Multiply A into the equivalent weight of the acid, B into that of the base, and divide the sum of the products by the sum of the equivalents: call the quotient D . Subtract C from D and multiply by $100/D$. The percentage loss or gain of electromotive force thus obtained represents in the author's opinion the relative amounts of loss or gain of molecular energy which have occurred on the union of the acid and base.

The results of numerous experiments with various classes of substances are given in tabular form. When an acid and base neutralise each other, there is in almost all cases an increase of electromotive force. There is an increase in about four-fifths of the cases in which a carbonate is used to neutralise an acid. Very little change in the electromotive force is observed when salt solutions or acid solutions are mixed. Salts, on the other hand, when mixed with acids, show considerable changes.

Most of the solutions investigated contained 1 equiv. of substance dissolved in 100 mols. of water.

J. W.

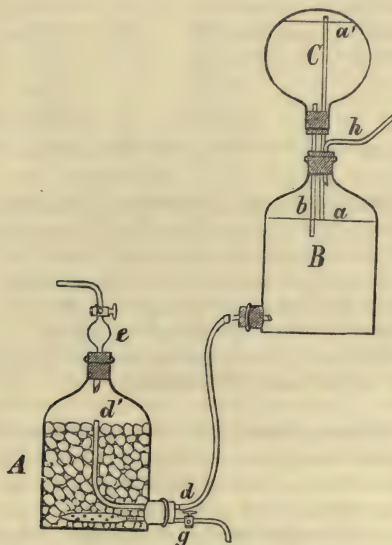
Use of certain Colouring Matters for the Determination of Affinities. By W. SPITZER (*Pflüger's Archiv*, 50, 551—573).—It has been noticed that the neutral and many acid salts of organic acids have an alkaline reaction towards lacmoïd, so that obviously a division of the alkali between the organic acid and the lacmoïd takes place. It may be assumed that this division will follow the Guldberg-Waage law of mass action, and will depend on the relative affinities of the acid and the lacmoïd for the alkali, so that by comparing the affinities of different acids with that of lacmoïd, it should be possible to obtain relative numbers for the affinities of the acids themselves. This the author has done for a number of organic acids, and obtained results which are in very fair accordance with those calculated from Ostwald's experiments on the affinities of the same acids, determined by their rate of hydrolysis of cane sugar and of methyl acetate, and by the electrical conductivities. The above method, therefore, may be regarded as leading to correct results. The importance of a knowledge of the affinities of the organic acids for a correct interpretation of those physiological changes in which such acids take part is pointed out.

H. C.

Rate of Evaporation of Solutions of Sodium and Potassium Chlorides. By P. LESAGE (*Compt. rend.*, 115, 473).—The author finds by direct experiment that pure water evaporates more rapidly than aqueous solutions of sodium or potassium chloride, and that solutions of potassium chloride evaporate more rapidly than solutions of sodium chloride of the same concentration. These results agree with Wüllner's determinations of the vapour pressures of these liquids.

C. H. B.

A Continuous Gas Evolution Apparatus. By A. V. KALEC-SINSZKY (*Zeit. anal. Chem.*, **31**, 544—548).—The modifications in the principle of Deville's and Kipp's apparatus are that the acid which has once passed from the reservoir *B* into the generator *A* becomes there fully neutralised, and can never be driven back into the reservoir, but is drawn off at the tap *g*, so that the acid when it is



brought into contact with the solid reagent is always fresh and of full strength. Further, the use of the Mariotte's flask *C* maintains the level of the acid in *B*, and the resulting pressure, constant. Any gas evolved after the tap *e* is closed escapes through *B* and by *h*, which should, therefore, be carried into a chimney. M. J. S.

Inorganic Chemistry.

Vapour Density of Halogen Hydrides at Low Temperatures. By H. BILTZ (*Zeit. physikal. Chem.*, **10**, 354—362).—It has been repeatedly shown that the vapour density of hydrogen fluoride at low temperatures (below 26°) corresponds with the molecular formula H_2F_2 , and not with the simple formula HF . In order to ascertain if the same tendency to the formation of double molecules exists in the corresponding halogen compounds, the author has determined their vapour density at low temperatures, using the

apparatus of V. Meyer and Goldschmidt (*Ber.*, 15, 1161), with slight modifications. His results show that no such tendency exists.

	Temperature.	Vapour density.	
		Found.	Calculated for HX.
Hydrogen chloride	-77°	1·197	1·258
Hydrogen bromide	-15	2·989	2·770
" "	-28	2·873	"
Hydrogen iodide	-17	4·569	4·423
" "	-25	4·619	"

J. W.

Oxidation of Solutions of Hydrogen Sulphide. By SALAZAR and NEWMANN (*Bull. Soc. Chim.* [3], 7, 334—336).—The authors' experiments show, in opposition to those of Lindo (*Abstr.*, 1888, 750), that solutions of hydrogen sulphide in the mixture of glycerol and water (equal parts), proposed by Lepage (*J. Pharm.*, 1867), undergo less change on keeping than do those in water. Furthermore, the oxidation of hydrogen sulphide in solutions of the gas proceeds more rapidly in diffused light than in darkness.

A. R. L.

Influence of Nitric Peroxide on the Specific Gravity of Nitric Acid. By G. LUNGE and L. MARCHLEWSKI (*Zeit. angew. Chem.*, 1892, 10—12; 330—331).—The authors have found that the results obtained when determining the strength of nitric acid by its specific gravity will be too high when the acid contains nitric peroxide. They have now constructed tables which give the corrected specific gravity when the amount of nitric peroxide is known. This is best estimated by delivering the nitric acid from a burette into a standard solution of potassium permanganate until the latter is quite decolorised.

When titrating nitric acid which contains nitrous acid, using methyl-orange as indicator, the latter should not be added until the acid is practically neutralised.

L. DE K.

Behaviour of Nitric Oxide at High Temperatures. By F. EMICH (*Monatsh.*, 13, 615—622; compare *Abstr.*, 1892, 940).—After discussing a question of priority, the author describes an apparatus he employs for determining to what extent decomposition occurs when nitric oxide is heated at various temperatures in porcelain tubes. Langer and Meyer's statement, that nitric oxide remains unchanged when heated at 900° and 1200°, is shown to be an error. In fact, as stated by Berthelot (*Compt. rend.*, 77, 1448), decomposition occurs when the gas is heated to a feebly glowing heat, such as will cause the containing tube to appear red in a darkened room.

G. T. M.

A Crystallised Compound of Arsenious and Sulphuric Anhydrides. By R. PEARCE (*Zeit. Kryst. Min.*, 20, 632; from *Proc. Colorado Sci. Soc.*, 3, 255—256).—In 1868, the author described

a crystallised compound of arsenious and sulphuric anhydrides derived from a calcining kiln in Swansea. Since then he has observed the same compound at the Argo Smelting Works in Colorado. It occurred some 3 feet under the uppermost part of the hearth in fine groups of large crystals encrusting lumps of slag. The crystals are of a complicated form, apparently monoclinic, with a pearly to adamantine lustre, a white colour, and a perfect cleavage. Analysis yielded:—

As_2O_3 .	SO_3 .	SiO_2 and loss.	Total.
68·22	28·91	2·87	100·00

B. H. B.

Carbonic Anhydride in the Air. By A. PETERMANN and J. GRAFTIAU (*Chem. Centr.*, 1892, ii, 201).—The amount of carbonic anhydride has been determined daily during two years in the air taken from the open country near Gemploux, a small Belgian town. In the average, it is 2·944 vols. per 10,000; in the town itself 3·70. It was estimated by aspirating the air through standard baryta, and determining the excess of the latter by means of oxalic acid. The amount of carbonic anhydride present is not affected by the direction of the wind, or by its blowing off the sea or from the land. Rain, quantity of moisture in the air, ordinary variations of temperature (from -5° to $+25^\circ$) and pressure, and the change of season, are equally without effect. Mist and snow, however, produce an increase; so does an unusual barometric depression, especially when accompanied by a strong sea breeze and a very low temperature; a very high temperature produces a diminution.

C. F. B.

Rubidium and Potassium Trihalides. By H. L. WELLS and H. L. WHEELER (*Amer. J. Sci.* [3], 43, 475—487).—The discovery of a series of caesium trihalides (*Abstr.*, 1892, 773), has led the authors to investigate the analogous rubidium and potassium compounds. The following table gives a list of the salts which they have been able to prepare, together with a list of the caesium series for comparison:—

CsI, I_2 ,	RbI, I_2 ,	KI, I_2 ,
CsBr, I_2 ,	—	—
CsBr, BrI ,	RbBr, BrI ,	KBr, BrI ,
CsCl, BrI ,	RbCl, BrI ,	—
CsCl, ClI ,	RbCl, ClI ,	KCl, ClI ,
CsBr, Br_2 ,	RbBr, Br_2 ,	—
CsCl, Br_2 ,	RbCl, Br_2 ,	—
CsCl, ClBr .	RbCl, ClBr .	—

The compound KI, I_2 had been previously obtained by G. S. Johnson (this Journal, 1877, i, 249). The failure to prepare the one member lacking in the rubidium series is due, no doubt, to the comparative instability of this series. In the potassium series only those salts could be prepared which correspond with the more stable caesium and rubidium compounds. The authors describe in considerable detail the method of preparation of these compounds, and discuss their

colour, stability, fusibility, and behaviour with solvents, whilst their crystallography is fully described in an appendix by S. L. Penfield.

B. H. B.

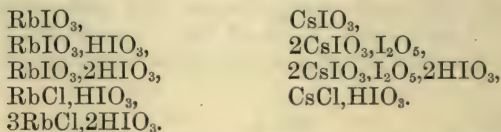
Pentahalides of the Alkali-metals. By H. L. WELLS and H. L. WHEELER (*Amer. J. Sci.* [3], **44**, 42—49).—From the peculiar behaviour of caesium tribromide and tri-iodide observed in their previous investigations, the authors concluded that a still higher bromide and iodide existed. These they have now identified as pentahalides. A description is given of the methods adopted for preparing the following compounds:— CsI_5 , CsBr_5 , $\text{CsCl}_3\text{Cl}_3\text{I}$, $\text{RbCl}_3\text{Cl}_3\text{I}$, $\text{KCl}_3\text{Cl}_3\text{I}$, $\text{NaCl}_3\text{Cl}_3\text{I}$ + $2\text{H}_2\text{O}$, and $\text{LiCl}_3\text{Cl}_3\text{I}$ + $4\text{H}_2\text{O}$. The crystallography of these compounds is described by S. L. Penfield. The compound $\text{KCl}_3\text{Cl}_3\text{I}$ was described in 1839 by Filhol. The sodium and lithium analogues of this compound differ from all the other polyhalides studied by the authors inasmuch as they contain water of crystallisation.

B. H. B.

Cæsium and Rubidium Aurochlorides and Aurobromides. By H. L. WELLS and H. L. WHEELER (*Amer. J. Sci.* [3], **44**, 157—162).—The compounds that have been prepared are CsAuCl_4 , $2\text{CsAuCl}_4 + \text{H}_2\text{O}$, CsAuBr_4 , RbAuCl_4 , and RbAuBr_4 . Their study was undertaken in the hope that some crystallographic analogy might exist between them and the alkali pentahalides described by the authors. No such analogy has been found; but, as some of these gold salts have never been described, an account is given of their preparation, properties, methods of analysis, and, in an appendix by S. L. Penfield, of their crystallography.

B. H. B.

Cæsium and Rubidium Iodates. By H. L. WHEELER (*Amer. J. Sci.* [3], **44**, 123—133).—The author has prepared the following new compounds:—



The method of analysis adopted is described, and crystallographical descriptions of the various compounds are furnished by S. L. Penfield.

The results of the investigations of the rubidium salts show that the normal iodate is the only one of the series that can be recrystallised unaltered from an aqueous solution. In the case of the caesium salts, the normal iodate and the salt $2\text{CsIO}_3 \cdot \text{I}_2\text{O}_5$ are not decomposed by water. The latter salt, and not the normal iodate, is given by the other caesium salts when recrystallised from water.

B. H. B.

Cæsium-Mercury Halides. By H. L. WELLS (*Amer. J. Sci.* [3], **44**, 221—236).—After enumerating all the previously-described mercury double halides containing the alkali metals or ammonium, the author describes the mode of preparation of the following salts:—

I.	II.	III.
Cs_3HgCl_5 ,	Cs_2HgCl_4	CsHgCl_3 ,
Cs_3HgBr_5 ,	Cs_2HgBr_4 ,	CsHgBr_3 ,
Cs_3HgI_5 ,	Cs_2HgI_4 ,	CsHgI_2 ,
$\text{Cs}_3\text{HgCl}_3\text{Br}_2$,	$\text{Cs}_2\text{HgCl}_2\text{Br}_2$,	CsHgClBr_2 ,
$\text{Cs}_3\text{HgBr}_3\text{I}_2$.	$\text{Cs}_2\text{HgBr}_2\text{I}_2$,	CsHgBrI .
	$\text{Cs}_2\text{HgCl}_2\text{I}_2$.	
IV.	V.	VI.
	CsHg_2Cl_5 ,	$\text{CsHg}_5\text{Cl}_{11}$,
$\text{Cs}_2\text{Hg}_3\text{I}_8$.	CsHg_2Br_5 ,	
	CsHg_2I_5 ,	
	$\text{CsHg}_2\text{ClBr}_4$.	$\text{CsHg}_5\text{ClBr}_{10}$.

One of these compounds, Cs_2HgCl_4 , had already been prepared by Goddeffroy. The results of the work on the cæsium-mercury salts fulfil the expectations concerning the value of cæsium as a means of studying alkali double halides, for all the previously-discovered types have been made with this metal, and one type besides (Cs_2HgHl_5) that had not hitherto been discovered. B. H. B.

Some Double Halides of Silver and the Alkali Metals. By H. L. WELLS and H. L. WHEELER (*Amer. J. Sci.* [3], **44**, 155—157).—During a systematic search for well-crystallised salts of the type $\text{M}'\text{X}, \text{AgX}$, three well-defined compounds of another type, $2\text{M}'\text{X}, \text{AgX}$, were obtained. The author's experience indicates that these 2 to 1 compounds are more easily prepared and crystallise better than the 1 to 1 compounds. The salts described are $2\text{CsCl}, \text{AgCl}$, $2\text{RbI}, \text{AgI}$, and $2\text{KI}, \text{AgI}$, of which the first two are believed to be new. Their preparation and properties, and the mode of analysis, are described, whilst crystallographical descriptions are furnished by S. L. Penfield. B. H. B.

Disruption of Silver Halides by Mechanical Force. By M. C. LEA (*Amer. J. Sci.* [3], **43**, 527—531).—Some years ago the author found that a latent image, capable of development, could be produced on a photographic plate by the action of mechanical force, such as tracing lines with a glass rod. He has now investigated the behaviour of the haloïd salts of silver under high pressure and under shearing stress.

Silver chloride and bromide, precipitated with an excess of the corresponding acid, and silver iodide, precipitated with an excess of potassium iodide, were dried by exposure to air in the dark, wrapped in bright platinum foil, and exposed for 24 hours to a pressure of 100,000 lbs. per square inch, applied gradually by means of a screw. All three silver salts darkened to a deep greenish-black. The platinum foil was not attacked, and hence the author concludes that the halogens are not set free, but react with the small quantity of moisture present, with formation of halogen acid. The change cannot be due to rise of temperature, because the pressure was

applied very gradually, and the silver salt was wrapped in platinum foil, and the latter was placed between large pieces of metal.

In order to ascertain the effect of shearing stress, pure silver chloride was triturated in a porcelain mortar in presence of a solution of tannin or a solution of sodium carbonate; in both cases it soon darkened.

The air-dried chloride was also triturated alone in a chemically-clean mortar, and after about 15 minutes trituration was perceptibly darkened, the colour increasing in intensity as the process was continued. The product was violet-purple, and agreed in its properties with silver photochloride.

These results show that the molecules of haloïd silver salts can be broken up by mechanical forces in the absence of active light, and they establish the uniformity of the action of all kinds of energy on these salts (compare Abstr., 1891, 803). Any form of energy is not only capable of producing a latent image susceptible to development, as shown in previous papers, but can also bring about the actual disruption of the molecules. It would seem, therefore, that the phenomena of the latent image and its development are not exclusively, nor even especially, connected with light. The disruption of the molecules of the silver salts by mechanical force is the more remarkable in view of the fact that the decomposition of all three salts is endothermic.

C. H. B.

Note by Abstractor.—The author claims that this is the first case of the mechanical decomposition of a compound formed by an exothermic reaction, but he seems to be unacquainted with Spring's experiments.

It is difficult to see how shearing stress (resulting from the sliding of one particle over another) was eliminated in those experiments where the air-dried salt was wrapped in platinum foil and compressed.

C. H. B.

Formation and Properties of Tetracalcium Phosphate. By O. FOERSTER (*Zeit. angew. Chem.*, 1892, 13—22).—Tetracalcium phosphate may be produced by boiling ordinary calcium phosphate with very strong aqueous potash, part of the phosphoric acid being abstracted; or it may be produced by strongly heating calcium triphosphate with lime or calcium carbonate. If, however, tricalcium phosphate is fused with solid potassium hydroxide, the mass insoluble in water will consist of calcium hydroxide, which may be readily dissolved with sugar solution, some calcium carbonate, and undecomposed or, perhaps, regenerated tricalcium phosphate.

It has now been proved beyond doubt that basic slags principally consist of tetracalcium phosphate. Their superior value as a manure is due to the fact that the tetracalcium compound is more readily decomposed in the soil than the tricalcium compound. Like dilute mineral acids, the acids contained in the soil rapidly abstract not only the extra molecule of lime, but also another, leaving the readily soluble dicalcium compound.

L. DE K.

Dissociation of Barium Peroxide. By H. LE CHATELIER (*Compt. rend.*, 115, 654—656).—Anhydrous barium oxide, obtained by strongly heating barium carbonate with carbon, does not combine with pure and dry oxygen at 500°. If, however, the oxide is heated in a current of air saturated with aqueous vapour at 20°, absorption of oxygen takes place very rapidly, the product being a liquid which only solidifies at 450°. This mixture contains 66·6 per cent. of barium hydroxide and 33·3 per cent. of the peroxide.

Barium peroxide was finally prepared by heating the somewhat-hydrated peroxide at 700° in a current of pure and dry oxygen so long as any water was given off. The product is not quite pure, but contains the minimum quantity of water necessary to ensure absorption of oxygen.

The pressures observed for a mean degree of decomposition are as follows :—

Temperature . . .	525°	555°	650°	670°	720°	735°
Pressure	20	25	65	80	210	260 mm.
Temperature	750°	775°	785°	790°		
Pressure	340	510	620	670 mm.		

The pressures are higher at the commencement of the decomposition, and lower towards the end.

The decomposition of barium peroxide by heat is a complex phenomenon. The presence of water vapour is essential, and it would seem that a fused mixture of barium peroxide and barium hydroxide is an indispensable intermediate compound. The pressure that limits the dissociation has a theoretical value infinitely great when the peroxide is saturated with oxygen, and no barium monoxide is present in any form. As the decomposition proceeds, however, the pressure decreases until sufficient monoxide is formed to exist in the solid state. Beyond this point, the pressure remains constant so long as any peroxide remains in the solid state. As soon, however, as the peroxide no longer exists except in a state of solution in the fused mixture, the pressure gradually decreases, and becomes nil when decomposition is complete. The importance of the degree of decomposition compatible with the maintenance of a constant pressure is higher the less the quantity of water present, but the establishment of a condition of equilibrium takes place more and more slowly. The period of constant pressure disappears when the proportion of water reaches a certain limit, which, at 450°, is 10 per cent., the mass being then completely fused.

The pressure of the water vapour contained in the oxygen is without influence on the pressure of the oxygen itself so long as barium monoxide and peroxide are present. The fused mixture, so long as excess of its constituents is present, has a constant composition at each temperature, and consequently the pressure of the water vapour is constant in the same sense as that of the oxygen. If the presence of water vapour in the air used for the regeneration of the barium peroxide has not exactly the proper value, there will be absorption or elimination of water, with a consequent alteration in the proportion

of the fusible substances. If there is too little moisture, combination with oxygen becomes impossible; if there is too much, all the peroxide melts and becomes useless.

C. H. B.

Phosphorescent Zinc Sulphide. By C. HENRY (*Compt. rend.*, 115, 505—507).—Phosphorescent zinc sulphide is obtained in large quantity by precipitating a neutral solution of pure zinc chloride with ammonia, redissolving the precipitate in excess of ammonia, and then exactly precipitating with hydrogen sulphide. The precipitate is carefully washed and dried, and is then heated almost to a white heat in a fire-clay crucible placed inside a plumbago crucible, brasqued with charcoal. The brilliancy of the phosphorescence seems to depend on the perfect purity of the zinc sulphide, and the product is either non-phosphorescent or feebly phosphorescent if zinc oxide or any zinc salt other than the chloride is used, or if alkali sulphides are used as the precipitant in place of hydrogen sulphide. Manganese sulphate, lead acetate, lithium carbonate, thallium carbonate, strontium chloride, basic bismuth nitrate, &c., all prevent phosphorescence.

The luminous intensity of the phosphorescence of the granular form of zinc sulphide, after excitation by the light from burning magnesium, is not less than 0.000215 of a candle-metre. The loss of light during the first 14 seconds is expressed by the formula $i_t = i_0 e^{-at}$ where i is the intensity of the light, and t is the time. The mean value of a , the velocity of emission, is 0.1970. The brightness of the sulphide in powder, when spread on a card, is represented by the equation $i^{0.5936}(t + 27.18) = 1647.5$; the results agreeing well with those of other observers.

C. H. B.

Simultaneous Precipitation of Copper and Antimony by the Galvanic Current. By W. HAMPE (*Chem. Zeit.*, 16, 417—418).—The author, who regularly examines samples of electrolytic copper, has as yet always found a small quantity of antimony, varying from 0.007 to 0.02 per cent. Although antimony is supposed not to come down until the last portions of copper are precipitated, the author has found that it precipitates together with the copper from the beginning of the electrolytic operation.

The amount of antimony will be reduced to a minimum by often changing the acid copper solution.

L. DE K.

A Limited Reaction. By A. COLSON (*Compt. rend.*, 115, 657—659).—When 10 grams of mercuric chloride is boiled with 500 c.c. of benzene previously dried by distillation over phosphoric anhydride, it partly dissolves, and if dry hydrogen sulphide is passed into the liquid, hydrogen chloride is liberated, and, after 20 hours, if all trace of moisture has been excluded, the yellow chlorosulphide, $\text{HgCl}_2 \cdot 2\text{HgS}$, is obtained. Similar phenomena are observed at the ordinary temperature. The limitation of the reaction is due to the formation of the molecular compound. It is not due to the retention of hydrogen chloride by the benzene, for if the chlorosulphide is introduced into the dry benzene along with fragments of sodium, it is practically unaltered even when treated with a current of hydrogen sulphide for

several hours. In presence of a trace of water, however, conversion of the mercuric salt into sulphide becomes complete.

Benzene solutions of mercuric salts react imperfectly with silicon sulphide, because the latter is insoluble in benzene. If, however, silicon sulphide is heated with mercuric chloride, silicon chloride is obtained together with mercuric sulphide; mercuric cyanide, under similar conditions, yields silicon cyanide as a yellow solid, soluble in water.

C. H. B.

Probable Presence of Iron Carbonyl in certain Illuminating Gas. By GUNTZ (*Bull. Soc. Chim.* [3], 7, 281—282).—The author noticed a deposit of ferric oxide on the cover glasses and porcelain reflectors of certain gas lamps which had been burning for some hours. He believes it to be due to the presence of iron carbonyl in the gas, this compound being probably formed by the interaction of the carbonic oxide contained in the gas and metallic iron which is used as a desulphurising agent.

A. R. L.

Note.—The author makes no mention of the similar observations of Roscoe and Scudder, on the probable presence of iron carbonyl in water gas (*Proc.*, 1891, 126), and of Thorne, as to its presence in coal gas which had been compressed in iron cylinders (*ibid.*).

A. R. L.

A Case of Solid Solutions. By E. A. SCHNEIDER (*Zeit. physikal. Chem.*, 10, 425—429).—When a solution of a sulphate containing a ferric salt is precipitated with barium chloride, a considerable quantity of iron is found in the barium sulphate in the form of ferric sulphate. The author finds that with varying quantities of barium sulphate and a constant quantity of iron, the volume of the solution being always the same, the relative quantity of iron in the precipitate is very nearly constant. With the same quantity of barium sulphate and varying quantities of iron, the amount of iron in the precipitate increases to a certain limiting proportion, and thereafter remains constant. The author considers that these results are very probably due to ferric sulphate being “dissolved” in the barium sulphate (compare Van’t Hoff, *Abstr.*, 1890, 1044).

J. W.

Dissociation of Chrome Alum. By H. BAUBIGNY and E. PÉCHARD (*Compt. rend.*, 115, 604—605).—A solution of chrome alum, even after repeated precipitation with alcohol, is always acid. 20 c.c. of a saturated solution, when treated with 0.03 gram of ammonia gas, is neutral to methyl-orange. After some time, the liquid deposits violet crystals, which have a distinctly acid reaction, whilst the mother liquor is also distinctly acid to methyl-orange. There is partial dissociation of the salt, and the condition of equilibrium is such that the liquid is acid. Chromium sulphate behaves in a similar manner, but ordinary alum and aluminium sulphate show no such behaviour, their solutions remaining neutral to methyl-orange for eight days.

C. H. B.

Atomic Weight of Palladium. By H. F. KELLER and E. F. SMITH (*Amer. Chem. J.*, 44, 423—434).—The metal was electrolytically

precipitated from an aqueous ammoniacal solution of pure palladiodiammonium chloride (compare Abstr., 1890, 831), and a full account is given of the special precautions taken in preparing this salt, which was made from commercial palladium containing copper, platinum, iridium, gold, and iron. Two series of experiments were made, the first consisting of three estimations, giving 106.920, with an extreme difference of 0.013, the second consisting of six estimations, giving 106.911, with an extreme difference of 0.070. The value deduced from the two series was 106.914 ($H = 1$, $N = 14.01$, $Cl = 35.37$). Keiser's value, 106.35 (Abstr., 1890, 17), obtained by reducing palladiodiammonium chloride in hydrogen, is deemed to be erroneous, partly owing to the impurity of the salt, and partly to the volatilisation of the metal and mechanical loss of the salt on heating. A number of experiments are quoted in confirmation of this view. By converting the palladammonium chloride into palladium sulphide by heating it in hydrogen sulphide, a value 107.07 was obtained, which the authors regard as confirming their other results.

JN. W.

Note.—Bailey and Lamb (Trans., 1892, 745) obtained 105.459 as the mean result of determinations by several methods.

Compound of Gold and Tin. By A. P. LAURIE (*Phil. Mag.* [5], 33, 94—99).—Matthiessen, from a study of the electric conductivity of alloys of gold and tin, concluded that there must exist three compounds of these metals with each other, for the conductivity curve showed three very sudden breaks, being shaped like a W. To these compounds he gave the formulæ Au_4Sn , $AuSn$, and Au_2Sn_3 respectively.

The author prepared a series of alloys of gold and tin, and investigated the electromotive force developed in a voltaic cell constituted as follows. In the inner cell a solution of gold chloride was contained, into which dipped a plate of pure gold. In the outer cell was a solution of stannic chloride, and into this a rod of the alloy was immersed. The results he obtained are exhibited in the following table:—

Percentage of tin in alloy.	E.M.F. in volts.
0	0.667
10.07	0.923
23.1	0.932
26.0	0.923
28.5	0.941
34.9	0.932
35.9	0.950
40.0	1.215
50.0	1.279
100.0	1.425

The values between 10 and 36 per cent. are constant, and evidently due to some definite compound of gold and tin, which determines the E.M.F. After 36 per cent. has been reached, the E.M.F. suddenly

risers; this would point to excess of tin being then present. The compound AuSn contains 37 per cent. of tin. No indication of Matthiessen's other compounds was obtained. J. W.

Mineralogical Chemistry.

Josephinite, a New Nickel-Iron. By W. H. MELVILLE (*Amer. J. Sci.* [3], 43, 509—515).—Magnetic pebbles have been discovered in large quantities in the gravel of a stream in Josephine and Jackson counties, in Oregon, in the vicinity of the district in which the well-known nickel silicate has been found. The pebbles are irregular in shape, and their smooth surfaces are coloured greenish-black, interrupted by bright areas of the greyish-white alloy of nickel and iron. This metallic portion is of special interest, in that it was found on analysis to consist of 23·22 per cent. of iron and 60·45 per cent. of nickel. This composition corresponds with the formula Fe_2Ni_5 . Evidence brought forward by the author points to the terrestrial origin of the pebbles described. For the new nickel-iron, the name of *josephinite* is proposed, in honour of the county in which it has been discovered. B. H. B.

Polybasite and Tennantite from Aspen, Colorado. By S. L. PENFIELD and S. H. PEARCE (*Amer. J. Sci.* [3], 44, 15—18).—At the Mollie Gibson mine, one of the most productive mines in Colorado, the most abundant silver mineral is polybasite, which occurs massive with greyish-black colour and irregular fracture. This massive polybasite is not a pure mineral, as at first sight it appears to be. Some of the polybasite crystals are surrounded by a layer of siderite, then by a narrow zone of metallic mineral, and then again by siderite. As this seemed to be the nearest approach to the pure crystallised silver mineral, an analysis of it was made, with the following results:—

S.	As.	Sb.	Ag.	Cu.	Zn.	Pb.	FeCO_3 .	MnCO_3 .	Total.
17·42	6·10	0·26	49·51	12·92	2·45	10·58	0·46	0·13	99·83

These results do not agree with those obtained on analysing the massive mineral, but after deducting 12·81 per cent. of impurities in the analysis quoted, and 28·18 per cent. in the second analysis, both give ratios almost exactly those required by the formula $9\text{Ag}_2\text{S As}_2\text{S}_3$.

Along with the polybasite, patches of steel grey tennantite are met with. On analysis, this mineral yielded results corresponding with the formula $4\text{Cu}_2\text{S, As}_2\text{S}_3$. The sp. gr. of the mineral is 4·56.

B. H. B.

Plattnerite from Idaho. By W. S. YEATES and E. F. AYRES (*Amer. J. Sci.* [3], 43, 407—412).—Plattnerite was regarded as a doubtful species until, in 1886, E. Kinch (*Abstr.*, 1887, 451) described a well-authenticated specimen from Leadhills, Scotland. Since then

analyses of plattnerite, from Idaho, have been published by H. A. Wheeler (Abstr., 1890, 339), and by J. D. Hawkins (Abstr., 1890, 340). In the meantime, a considerable quantity of this material has been secured from a tunnel near Mullan, in Idaho. The plattnerite occurs in botryoidal nodules embedded in a mixed ochre of limonite and plattnerite. Its hardness is 5·5, and its sp. gr. 8·56. Analysis yielded:

Pb.	Ag.	Cu.	Fe,Al.	O.	Insoluble.	Total.
83·20	trace	0·14	1·20	12·93	0·82	98·29

Impurities being neglected, the mineral thus contains 86·55 per cent. of lead and 13·45 per cent. of oxygen. A crystallographical description of the mineral is given by E. F. Ayres. The crystals are tetragonal, and isomorphous with rutile (TiO_2), cassiterite (SnO_2), and polianite (MnO_2), minerals which have a similar composition.

B. H. B.

Penfieldite, a New Mineral Species. By F. A. GENTH (*Amer. J. Sci.* [3], 44, 260—261).—With minerals formed by the action of sea-water on ancient slags at Laurion, Greece, the author found a very few hexagonal crystals of a new mineral, for which he proposes the name of *penfieldite* in honour of S. L. Penfield. The crystals are white, and contain 18·55 per cent. of chlorine and 78·25 per cent. of lead. The formula is therefore $\text{PbO}, 2\text{PbCl}_2$.

B. H. B.

The Clinton Iron Ore. By C. H. SMYTH, Jun. (*Amer. J. Sci.* [3], 43, 487—496).—The author proposes to place the Clinton hæmatites in the category of original chemical deposits of date coeval with the enclosing strata. This result he bases on a careful study of this ore at the typical locality, Clinton, New York, his conclusion being that the oölitic ores at Clinton are not of secondary origin, but were deposited as hydrated ferric oxide in intimate connection with contemporary deposition of amorphous and chalcedonic silica. Hitherto the theory of pseudomorphous replacement of limestone has been generally accepted to explain the formation of the Clinton ore.

B. H. B.

Fluorine in Fossil Wood. By T. L. PHIPSON (*Compt. rend.*, 115, 473—474).—Thirty years ago the author found, in the Isle of Wight, a specimen of fossil wood that contained 32·45 per cent. of phosphoric acid and 3·9 per cent. of fluorine. The wood was found in cretaceous grit, and seemed to have been fossilised by calcium phosphate and calcium fluoride. It had a brown colour and woody structure, and was sectile; sp. gr. = 2·17.

C. H. B.

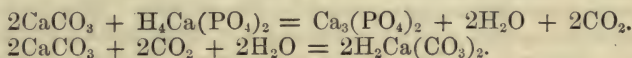
Herderite from Hebron, Maine. By H. L. WELLS and S. L. PENFIELD (*Amer. J. Sci.* [3], 44, 114—116).—The authors describe a new and interesting variety of herderite, almost free from fluorine. It consisted of a few yellowish-white crystals on albite, in form closely resembling those of childrenite. On analysis, it yielded the following results:—

P ₂ O ₅ .	FeO.	CaO.	H ₂ O.	F.	Insoluble.
40·81	15·32	32·54	5·83	0·40	5·27

The result confirms the idea advanced by Penfield and Harper, that fluorine and hydroxyl are mutually replaceable in herderite, and the formula deduced by them for the mineral is confirmed.

B. H. B.

Formation of Phosphate Nodules. By C. L. REESE (*Amer. J. Sci.* [3], 43, 402—406).—It having been suggested that the South Carolina phosphates may have been formed by the action of swamp waters lying on beds of marl, the author has made a series of experiments to test the accuracy of this view. From his experiments, it certainly seems probable that both carbonic acid and the humus substances in fresh-water swamps play an important part in the accumulation and concentration of calcium phosphate. The marls, in the first place, contain a small percentage of phosphate, which would gradually be increased as the carbonate is removed. The changes taking place may be represented by the following equations:—



The humus substances also give off carbonic anhydride on decomposition, and there is thus a further cause for concentration from this source.

B. H. B.

New Occurrence of Ptilolite. By W. CROSS and L. G. EAKINS (*Amer. J. Sci.* [3], 44, 96—101).—In 1886, the authors described (Abstr., 1866, 990) the first occurrence of a new hydrous aluminium, calcium, and alkali silicate, to which they gave the name of ptilolite. They now describe a new occurrence of this mineral near Silver Cliff, Custer Co., Colorado.

On analysis, this mineral yielded

SiO ₂ .	Al ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
67·83	11·44	3·30	0·64	2·63	13·44	99·28

The empirical formula derived from this analysis is $\text{R}'\text{Al}_2\text{Si}_{10}\text{O}_{24} + 6\frac{2}{3}\text{H}_2\text{O}$, which is the same as that of mordenite, but, as Pirsson has already pointed out (Abstr., 1891, 276), the two minerals are physically unlike.

B. H. B.

Constitution of Ptilolite and Mordenite. By F. W. CLARKE (*Amer. J. Sci.* [3], 44, 101—102).—The data given by Cross and Eakins (see preceding abstract) lead to simple formulæ for the minerals under discussion. When it is recognised that part of the water in each mineral may be basic, the apparent anomalies disappear, and the compounds reduce at once to similar salts of the acid $\text{H}_2\text{Si}_2\text{O}_5$, an acid well known in the species petalite and milarite. Both ptilolite and mordenite become represented by the general formula $\text{Al}_2(\text{Si}_2\text{O}_5)_n\text{R}'_4 + n\text{H}_2\text{O}$; the only serious uncertainties being in respect to the hydration.

B. H. B.

Constitution of certain Micas and Chlorites. By F. W. CLARKE and E. A. SCHNEIDER (*Amer. J. Sci.* [3], 43, 378—386).—The authors have received from the Curator of Minerals in the Imperial School of Mines in St. Petersburg, some highly important material bearing on their researches (Abstr., 1891, 529). These five specimens, on which the present paper is founded, are as follows:—(1) Walnewite, from the Ural; (2) clinochlore from the same locality, the Nikolai-Maximilian mine; (3) leuchtenbergite from Slatoust, Ural; (4) diallage serpentine from Sysstert, Ural; and (5) white mica from Miask, Ural. From the analyses given of these minerals, the authors deduce the following empirical formulæ:—

Walnewite	$\text{Al}_{86}\text{Mg}_{76}\text{H}_{50}(\text{SiO}_4)_{18}\text{O}_{174}$.
Clinochlore	$\text{Al}_{38}\text{Mg}_{87}\text{H}_{143}(\text{SiO}_4)_{52}\text{O}_{113}$.
Leuchtenbergite	$\text{Al}_{42}\text{Mg}_{86}\text{H}_{143}(\text{SiO}_4)_{56}\text{O}_{121}$.
Serpentine	$\text{Al}_4\text{Mg}_{102}\text{H}_{135}(\text{SiO}_4)_{71}\text{O}_{35}$.
Mica	$\text{Al}_{75}\text{K}_{23}\text{H}_{46}(\text{SiO}_4)_{74}\text{O}_2\text{F}_5$.

The last of these minerals is evidently an ordinary muscovite. The others were examined in great detail by the authors. The clinochlore and leuchtenbergite are typical members of Tschermak's orthochlorite series (this vol., ii, 19); which, according to him, are mixtures of two end compounds, serpentine and amesite. How amesite behaves on ignition is not known; but serpentine splits up into olivine and enstatite. According to Tschermak's theory, a clinochlore of the composition SpAt should yield, on ignition, 18 per cent. of enstatite. Since no enstatite is actually formed, it is plain that the clinochlore and leuchtenbergite examined contain no serpentine molecules, and hence Tschermak's theory falls to the ground. The formation of spinel from the walnewite and the chlorites seems to follow a single quantitative law. If the spinel is deducted from the composition of each mineral, the soluble portion may be expressed as a mixture of olivine and magnesian garnet. That these minerals are actually formed is not proved; but it seems highly probable that the chlorites studied do split up, yielding water, spinel, garnet, and olivine as the final products of decomposition.

B. H. B.

Quartz Boulder in Ohio Coal. By E. ORTON (*Amer. J. Sci.* [3], 44, 62—63).—It is well known that boulders are occasionally met with in coal seams. In the United States, Ohio has furnished the largest number of cases. These have all been derived from a single coal seam, the Middle Kittanning seam. The author now describes a boulder recently discovered in the Sharon seam, the lowest of the series. It is noteworthy in that it is not a metamorphic sandstone or quartzite like those previously found, but is an excellent example of vein quartz, and it has not been worn by water or glacial action, but is as angular as if freshly broken from the parent mass.

B. H. B.

Augite and Plagioclase in a Minnesota Gabbro. By W. S. BAYLEY (*Amer. J. Sci.* [3], 43, 515—520).—The author describes a fibrous growth around olivine, which resembles very strongly the

reaction rims that have been described as existing between olivine and plagioclase. A careful study of the phenomenon, however, disclosed the fact that the growth is not due to reactionary processes between the rock's constituents, but is simply an original intergrowth of two of them, it being, in fact, a granophyric aggregate of plagioclase and augite. The major portion of the latter mineral in the rock separated before the felspar, and fastened upon the surfaces of the already formed olivine and magnetite. In many cases, however, before the crystallisation of the augite had ceased, the felspar began to form, and the two minerals crystallised together.

B. H. B.

Mica-peridotite from Kentucky. By J. S. DILLER (*Amer. J. Sci.* [3], 44, 286—289).—The author describes an eruptive rock from the Flanary Dyke, Crittenden Co., Kentucky. It is composed essentially of biotite, serpentine, and perovskite, with a smaller proportion of apatite, muscovite, magnetite, chlorite, calcite, and other secondary products. An analysis of the rock is given by the author, the results showing that, although belonging to the peridotites, this rock cannot be included in any of Rosenbusch's six types. Hitherto no peridotite rock has been recognised in which biotite is an original essential constituent, and the author, therefore, suggests for the Flanary Dyke rock the name of mica-peridotite.

B. H. B.

Meteorite Iron from Hassi Iekna, Algeria. By S. MEUNIER (*Compt. rend.*, 115, 531—533).—This meteorite, the fall of which was observed by some Arabs, is a mass of iron weighing 1250 grams. Its contours are rounded, and it is covered with a black crust of a uniform thickness of 0.5 mm. The interior is very coherent, and has in some parts a fibrous structure; a polished surface shows well-marked Widmannstätten figures when treated with hydrochloric acid. The mass consists essentially of a mixture of kamacite, Fe_{24}Ni , and plessite, Fe_{10}Ni , but contains lamellæ of schreibersite, and some pyrrhotine or troilite; its sp. gr. is 7.67 at 14°, and its composition is Fe, 91.32; Ni, 5.88; Co, 0.81; Cu, traces; S, traces; insoluble residue, 1.04 = 99.05.

The Hassi Iekna meteorite belongs to the rare lithological type described by the author, in 1870, under the name of schweztzite.

C. H. B.

New Meteorite from Kentucky. By H. L. PRESTON (*Amer. J. Sci.* [3], 44, 163—164).—In August, 1889, a meteorite was found in Kenton Co., Kentucky, interlocked in the roots of an ash tree 14 inches in diameter, at a depth of $3\frac{1}{2}$ feet below the surface. It is a meteorite of the siderite variety, measuring 21 by 14 by 8 inches in its greatest diameters, and weighing $359\frac{1}{2}$ lbs. It has numerous shallow pittings, and is entirely free from crust. On analysis, it gave the following results:—

Fe.	Ni.	Co.	Cu.	C.	S.	P.	Total.
91.59	7.65	0.84	trace	0.12	trace	trace	100.20

B. H. B.

Meteorite from Central Pennsylvania. By W. G. OWENS (*Amer. J. Sci.* [3], 43, 423—424).—This meteorite was found on September 25, 1891, upon the east side of Bald Eagle Mountain, Williamsport, Pennsylvania. It weighs 7 lbs. 1 oz., and resembles in general outline a human foot. It is pitted deeply, and is covered with a reddish-brown rust. Its sp. gr. is 7·06. When polished, and etched with dilute acid, the Widmannstätten lines appeared very distinctly. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	S.	Si.	Total.
91·36	7·56	0·70	0·09	0·06	trace	99·77

The meteorite could not have been of recent fall, as it was found covered with several feet of stones, and, as far as can be learned, it is the only specimen of the fall which has been found. B. H. B.

Meteorite from Indian Valley Township, Virginia. By G. F. KUNZ and E. WEINSCHENK (*Amer. J. Sci.* [3], 43, 424—425).—In the spring of 1891, a mass of meteoric iron was turned up by a plough in Indian Valley township, Floyd Co., Virginia. It weighs 31 lbs., and measures 11 by 8 by 5 inches. The surface is much corroded, and covered with a limonite crust. Analysis gave the following results:—

Fe.	Ni.	Co.	Cu.	P.	S.	Si.	Total.
93·59	5·56	0·53	trace	0·27	0·01	trace	99·96

The structure of this meteorite is very interesting, as it lies between the so-called breccia and hexahedral irons. Some parts of the mass exhibit a granular structure, identical with that of the Chattooga meteoritic iron. It is a question whether the granular structure is the original structure out of which hexahedral particles were formed through recrystallisation, or whether it is due to the fact that this iron, not being rich in nickel, has a lack of crystallising power.

B. H. B.

Meteorite from the Sierra de la Ternera, Chili. By G. F. KUNZ and E. WEINSCHENK (*Amer. J. Sci.* [3], 43, 425—426).—This meteorite was found in the Sierra de la Ternera, Province of Atacama, Chili. Although small, weighing but 650 grams, it is undoubtedly the entire meteorite, as the unbroken original crust shows. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	Total.
83·02	16·22	1·63	0·00	100·87

This analysis places the iron near the Cape Iron group; but as the physical properties of this group of irons have been so little studied, it is impossible to say whether the structure coincides or not. The complete absence of phosphorus indicates that this meteorite is an exception to the rule, in not containing the characteristic phosphor-nickel iron.

B. H. B.

Zinc-bearing Spring Waters from Missouri. By W. F. HILLEBRAND (*Amer. J. Sci.* [3], **43**, 418—422).—Zinc salts have been observed in inconsiderable quantities in certain springs in the south of France and New Zealand; but the spring waters described by the author are, it is thought, unique, in that their chief saline constituent is zinc sulphate. On the road from Joplin to Seneca, in Newton Co., Missouri, there is a series of springs varying in size, and discharging from $\frac{1}{2}$ gallon to 3 gallons of water per minute. On analysis, the water from two of these springs was found to yield, respectively, 297.7 and 327.0 parts of zinc sulphate in 1,000,000. The source of the metallic salt constituents of these waters is, of course, to be sought in one of the deposits of zinc-blende so numerous in Missouri, although there is no known indication of zinc ores within a quarter of a mile of the springs.

B. H. B.

Physiological Chemistry.

Respiration in Fishes. By C. DUNCAN and F. HOPPE-SEYLER (*Zeit. physiol. Chem.*, **17**, 165—181; see this vol., ii, 63).—The respiratory changes in fishes and other water-breathing animals was investigated in perch, trout, cray-fish, &c., by means of an apparatus modified from the ordinary forms of respiratory apparatus to suit the exigencies of the case. The apparatus is figured and fully described. In all cases, a control experiment with a mammal (rabbit) was carried on simultaneously.

The results, fully given in tabular form, come into three categories; in the first, there were from 3 to 4 c.c. oxygen per litre of water. A corresponding atmosphere, containing 8 to 11 per cent. of oxygen, was used for the rabbit; and both fish and rabbit got on well.

In the second group, the oxygen was reduced to 0.8—1.7 c.c. per litre, and the percentage for the rabbit to 2—4.5 per cent., in the air it was breathing. The rabbit and the fish both get dyspnoea, and, if left there long, die.

In the third set of experiments (0.7—0 c.c. oxygen for the fish), they soon turn over on their sides and die.

W. D. H.

Dextrose in Blood. By M. PICKARDT (*Zeit. physiol. Chem.*, **17**, 217—219).—The blood is best freed from proteids and pigment by zinc acetate (Abeles, *Abstr.*, 1891, 1399). It then is found to contain a substance which is fermentable with yeast, is dextrorotatory, and reduces Fehling's solution. The proof that this substance is dextrose is afforded by the phenylhydrazine test.

W. D. H.

Fluorine in Bones and Teeth. By S. GABRIEL (*Zeit. anal. Chem.*, **31**, 522—525).—The estimations made by Carnot (*Abstr.*, 1892, 911) have given the following percentages of calcium fluoride in bones:—

Shaft of human shank bone	0.35 per cent.
Head of ditto	0.37 "
Leg bone of ox	0.45 "
Bone of sea-cow	0.63 "
Leg bone of elephant.....	0.47 "
Tooth of ditto.....	0.43 "
Tusk of ditto	0.20 "

The author, relying on the etching test, finds, indeed, traces of fluorine in the ash of ox teeth, but the indications are quite insignificant compared with those obtained from mixtures of bone ash with 0.2 per cent. of calcium fluoride, whence he concludes that the above, and all hitherto published numbers, are far too high. At the same time, his complete analyses always show a deficit of about 1 per cent., although several methods of analysis have been employed, and, as this deficiency cannot all be fluorine, he suggests the possibility of the presence of some element not hitherto observed. M. J. S.

The Relation of the Urinary Carbohydrates to Humous Substance. By E. SALKOWSKI (*Zeit. physiol. Chem.*, 17, 229—273).—The present article is largely polemical, and the author reaffirms his older view (with some new experiments), that the fatty acids (especially acetic) which are found in putrid urine originate from the carbohydrates of normal urine. These are two in number, dextrose and animal gum.

That the acids originate from humous substances, or that the humous substances originate from carbohydrates, is considered very doubtful; the humous substances in the urine increase on standing, but this appears to be independent of putrefaction. The amount of reducing substance is much greater than the humous substances will account for. The method adopted for the estimation of the carbohydrates is Baumann's method with benzoic chloride; Udranszky's method for estimating humous substances is used. Urine, freed from humous substances by long-continued heating with hydrochloric acid behaves like normal urine. W. D. H.

Alcaptonuria. By H. EMBDEN (*Zeit. physiol. Chem.*, 17, 182—192).—A case of alcaptonuria is recorded, in which the disorder had been present, apparently, throughout life, and in which other members of the same family suffered similarly.

Alcapton was described by earlier authors as catechol, or proto-catechuic acid, by Kirk as uroleucic acid (trihydroxyphenylpropionic acid), and by Baumann and Wolkow (*Abstr.*, 1891, 1128) as homogentisic acid. This substance probably originates from tyrosine, which, uniting with 5 atoms of oxygen, yields the acid in question, ammonia, carbonic anhydride, and water. How and when this unusual metabolic act occurs is to be the subject of further experiments. In the present case, homogentisic acid was the substance which occurred in the urine. W. D. H.

Poisoning by Hydrogen Sulphide. By USCHINSKY (*Zeit. physiol. Chem.*, 17, 220—228).—The toxic action of hydrogen sulphide has been recently investigated by Pohl (*Arch. exper. Path. Pharm.*, 22, 1) and Lehmann (*Arch. Hygiene*, 14, 135). They state that sodium sulphide is formed, which causes death by paralysis of the nerve centres, especially of the brain. Lehmann states that œdema of the lungs is also produced. This was not, however, found in the present research, which was almost entirely directed to ascertaining whether the gas acts as a hypnotic, as Schulz states (*Münch. med. Woch.*, 1892, No. 16). No evidence that it acts as such was found, and, therefore, the view that sulphonal produces its effects by giving off hydrogen sulphide in the body is untenable.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

A New Bacillus in Rain Water. By A. B. GRIFFITHS (*Bull. Soc. Chim.* [3], 7, 332—334).—The author has discovered in rain water, stored in an open barrel during a mild winter, a microbe which he names *Bacillus pluvialis*. When cultivated on gelatin plates, it forms yellow colonies 2—10 mm. in diameter. It liquefies gelatin, and develops rapidly when grown upon a piece of potato, colouring it orange, and transforming the starch into glucose. The colouring matter is soluble in alcohol, benzene, chloroform, ether, and carbon bisulphide, but insoluble in water. The microbe is a true bacillus, and is not formed from spores; it has a length of 2—4 μ and a breadth of 0.6—0.8 μ , and is stained by aniline colours. It can only live in water containing organic matter; the cultures may be dried, but are killed by heating at 100° for 15 minutes. The bacillus does not appear to be pathogenic. When cultivated for several days on peptonised gelatine, a *ptomaine*, $C_9H_{21}N_2O_5$, crystallising in white, clinorhombic, nacreous needles or prisms is formed; this compound has a slightly bitter taste and a neutral reaction, dissolves in 80 parts of water at 17°, and is very soluble in boiling water and in chloroform, fairly so in alcohol, but insoluble in ether. Its solutions give a white precipitate with sodium phosphomolybdate, a chestnut-coloured precipitate with Nessler's solution, and a yellow precipitate with tannin; its crystalline derivatives are the *hydrochloride*, the *platinochloride*, and the *aurochloride*. The *ptomaine* appears to be non-toxic, but acts as a powerful diuretic.

A. R. L.

Absorption of Atmospheric Nitrogen by Microbes. By BERTHELOT (*Compt. rend.*, 115, 569—574).—With a view to throw some light on the mechanism by which the absorption and fixation of atmospheric nitrogen is effected by microbes, the author has made experiments with natural humic acid extracted from soils in which

absorption of atmospheric nitrogen was known to take place, and with artificial humic acid prepared from sugar. In each case, about 5 grams of humic acid was placed in a flask containing about 6 litres of air, and was mixed with some distilled water and 2 c.c. of water containing lower forms of vegetation which had developed in presence of light in a flask of ordinary water. The flasks were then very carefully stoppered, and exposed to diffused light for several months. In every instance white, microscopic, vegetable growths of many species developed, and a certain quantity of carbonic anhydride was formed. With natural humic acid, there was an increase in the combined nitrogen of 0.0104—0.0156 gram, or from 6 to 9 per cent., of the nitrogen originally present in the humic acid. With the artificial acid, there was a slight absorption of nitrogen.

In one experiment with natural humic acid, extending over about nine months, the quantity of nitrogen absorbed was 0.0545 gram, or 30.3 per cent., of the quantity originally present in the acid.

C. H. B.

Absorption of Atmospheric Nitrogen by Plants. By T. SCHLOESING, Junr., and E. LAURENT (*Compt. rend.*, 115, 659—661).—The experiments in which the direct absorption of atmospheric nitrogen has been established were made with soils comparatively poor in nitrogen. The authors have therefore repeated some of these experiments, using soils rich in nitric nitrogen. Under these conditions, the plants develop much more vigorously, but no fixation of atmospheric nitrogen was observed in the case of oats, colza, grasses, or potatoes.

C. H. B.

Carbohydrates of the Coffee Berry. By E. E. EWELL (*Amer. Chem. J.*, 14, 473—476).—The portion of coffee insoluble in water contains, according to a communication made by Maxwell to the author, a substance which yields galactose under acid hydrolysis, and, according to Reiss (*Abstr.*, 1889, 687), a substance which yields mannose under that treatment. The soluble portion contains cane sugar, to demonstrate the presence of which, the ground coffee, deprived of its fat by treatment with ether, is extracted with 70 per cent. alcohol. The extract is treated with lead acetate, the excess of lead removed by hydrogen sulphide, and the sugar precipitated as saccharate by the addition of strontium hydroxide to the boiling solution. The saccharate is then suspended in water, the base precipitated by carbonic anhydride, the water replaced by alcohol, and the sugar finally crystallised from the latter solvent. The process may be simplified with advantage by omitting the precipitation with strontium hydroxide. The percentage of saccharose, as estimated from the reducing power of the extract after treatment with lead acetate, removal of the excess of lead, and inversion, was 6.29.

The insoluble portion of coffee yields furfuraldehyde when distilled with dilute hydrochloric acid (sp. gr. 1.06), and therefore contains carbohydrates of the pentose group. An average of 0.22 gram, or 4.4 per cent., of the aldehyde, corresponding with 9 per cent. of pentose, was obtained from 5 grams of untreated coffee.

When coffee is extracted with 5 per cent. aqueous sodium hydroxide,

and the extract treated with alcohol (as in the separation of xylan from wood), a gum is precipitated, which, after washing in succession with alcoholic hydrogen chloride, alcohol, and ether, and drying over sulphuric acid, forms a greyish, translucent, hard, brittle, friable mass. On hydrolysis, this yields a reducing substance, equivalent to 74.2 per cent. of dextrose; furfuraldehyde (13 per cent.), on distillation with dilute hydrochloric acid; mucic acid (18.7 per cent.), on oxidation with nitric acid; and but a slight ash (0.84 per cent.) on incineration. It is thus probably a compound, the molecule of which contains one pentose and one galactose group (compare Lintner and Düll, *Zeit. angew. Chem.*, 1891, 538; Lippmann, *Abstr.*, 1891, 284). The acid extract of coffee also yields furfuraldehyde and mucic acid.

JN. W.

Relations between Fat-decomposing and Glucoside-decomposing Ferments. By W. SIGMUND (*Monatsh.*, 13, 567—577).—The author has extended his previous work (*Abstr.*, 1890, 1455), and has examined the action both of glucoside-decomposing ferments and of oleaginous seeds, or the ferments contained in them, on glucosides. Emulsion and myrosin were chosen as representatives of the first class, and were found to have the power of hydrolysing olive oil to some extent. In the second series of experiments, amygdalin and salicin were mixed with either the triturated seeds of hemp, poppy, and rape, or emulsions prepared from them. That the glucosides had undergone hydrolysis under the influence of the ferments, was shown by the formation of hydrocyanic acid, benzaldehyde, and glucose from the amygdalin, and of saligenin and glucose from the salicin. This hydrolysis could not be induced by proteïd substances.

The author has further commenced an investigation of the hydrolysing power of the pancreas, and the results at present obtained appear to indicate that pancreatic juice is able to bring about the hydrolysis of the glucosides.

G. T. M.

An Acid from Beet Leaves. By E. O. v. LIPPMANN (*Ber.*, 25, 3220).—The author has identified as hydrocaffeic acid the acid which he formerly found (*Abstr.*, 1888, 262) to be present in traces in the autumn in the leaves of the beet.

L. T. T.

Nitrogenous Constituents of the Seedlings of *Vicia sativa*. By E. SCHULZE (*Zeit. physiol. Chem.*, 17, 193—216).—The following nitrogenous bases were found:—Asparagine, glutamine, leucine, amidovaleric acid, phenylalanine, traces of tyrosine, besides guanidine, choline, and betaine. The first six probably originate from proteïds; asparagine is the most abundant. Further experiments as to the origin of guanidine are necessary. Choline comes from lecithin, and betaine is present in the ungerminated seeds. Vicine is present in the ungerminated seeds also, but it disappears as germination proceeds.

W. D. H.

Analytical Chemistry.

Estimation of Hydrogen and Barium Peroxides. By A. BAUMANN (*Zeit. angew. Chem.*, 1892, 116—117).—From 2 to 5 c.c. of the solution of hydrogen peroxide is mixed in the author's apparatus with 10 c.c. of a saturated solution of potassium ferricyanide and afterwards with 5 c.c. of aqueous potash or soda. 1 c.c. of liberated oxygen equals 1.51862 milligrams of H_2O_2 . Barium peroxide is estimated as follows:—About 0.5 gram of the substance is introduced into the outer chamber of the generating vessel and dissolved in a small quantity of dilute hydrochloric acid (1 : 10), and then from 2 to 3 grams of potassium ferricyanide is added. The inner glass cylinder is next filled with 10 c.c. of strong aqueous soda (1 : 2), and after cooling for some time, the liquids are mixed and the volume of oxygen is read off. 1 c.c. of this gas equals 7.5564 milligrams of BaO_2 . L. DE K.

Estimation of Hydrochloric acid in the Contents of the Stomach. By A. KOSSLER (*Zeit. physiol. Chem.*, 17, 91—116).—An examination of the various methods adopted for estimating hydrochloric acid in the stomach contents led to the following results:—

Hoffmann's method (*Centr. klin. Med.*, 1889, No. 46) consists in estimating polarimetrically the amount of inversion produced in a solution of cane sugar; this is proportional to the amount of hydrochloric acid and the strength of the sugar solution, the temperature and duration of the experiment being constant. Later (*Verhand. internat. Med. Congress, Berlin*, ii, Abth. 5, 201), instead of the inversion of cane sugar, he adopted the hydrolysis of methyl acetate into methyl alcohol and acetic acid, the latter being estimated by titration. Both methods give very exact results when applied to the stomach contents; it does not, however, indicate how much of the hydrochloric acid is united to proteid.

Winter's method (*Bull. Méd.*, 1889, No. 95; 1890, Nos. 8 and 54) consists in taking three quantities of the stomach contents; the first is treated with excess of soda, evaporated to dryness, ignited, and the amount of chlorine estimated by titration with silver nitrate; the second specimen is evaporated to dryness and kept at 100° for an hour, after which it is treated like the first. The difference gives the amount of free hydrochloric acid. The third portion is ignited immediately and then the chlorine estimated. The difference between estimations 2 and 3 gives the quantity of hydrochloric acid united to organic substances and to ammonia. The values obtained for the free acid and that united to organic substances are too high; the source of error is that in evaporating, and incinerating, hydrochloric acid is formed from acid phosphates and chlorides of the alkaline earths.

Braun's method also yields too high results, as in his titration he reckons as hydrochloric acid the acidity of acid phosphates.

Leo's method (*Centr. Med. Wiss.*, 1889, No. 26) consists in neutralising free acid with calcium carbonate; he states that the acid phosphates present are not decomposed. The loss of acidity gives the

measure of free acid present. Wagner (*Pflüger's Archiv*, 50, 371) and others have criticised this method. It, however, gives fairly accurate results if organic acids are first removed by extraction with ether.

Sjöqvist's method (Abstr., 1889, 302) is, in the presence of phosphates, attended with loss of hydrochloric acid. W. D. H.

Gas-volumetric Estimation of Iodine and Acids. By A. BAUMANN (*Zeit. angew. Chem.*, 1892, 70—72).—The author, who is still engaged on the subject, has, some time ago, communicated an easy and accurate process for the gas-volumetric estimation of iodine and also of acids (Abstr., 1892, 103, 538). Attention is now called to the fact that the success of the operation depends on the celerity with which the liberated iodine is mixed with the alkaline solution of hydrogen peroxide. The latter substance should not be used in large excess and should be rendered alkaline with solution of potassium hydroxide (1 : 1) immediately before use, and must be cooled.

L. DE K.

Estimation of Nitric acid by its Specific Gravity. By G. LUNGE and L. MARCHLEWSKI (*Zeit. angew. Chem.*, 1892, 10—12, 330—331).—See this vol., ii, 66.

Estimation of Nitrogen in Sodium Nitrate. By ALBERTI and HEMPEL (*Zeit. angew. Chem.*, 1892, 101—104).—As commercial sodium nitrate often contains a considerable percentage of potassium nitrate, the author would like to abolish the present conventional process of estimating the moisture and the impurities and taking the nitrate by difference or refraction.

The direct estimation of the nitrogen in Chili saltpetre is most conveniently effected according to the process communicated by Ulsch (Abstr., 1892, 1518), or by Lunge's nitrometer. L. DE K.

Estimation of Nitrites. By J. GROSSMANN (*Chem. Zeit.*, 16, 818—819).—The author proposes the following simple process, which is based on the fact that if dilute sulphuric acid is added to a boiling solution of a nitrite, the reaction takes place according to the equation $3\text{NaNO}_2 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{NaNO}_3 + 2\text{NO} + \text{H}_2\text{O}$, and that, consequently, only two-thirds of the base is neutralised by the standard acid. To get correct results, the acid must not be standardised, as usual, with sodium carbonate, but with a pure nitrite. 3 grams of pure sodium nitrite is dissolved in a flask in 200 c.c. of hot water, and after adding 40 c.c. of normal sulphuric acid boiled, until all nitric oxide has been expelled, the excess of acid is then titrated with normal soda. The acid may now be used for the assay of any commercial nitrite, but as these generally contain some free alkali, this must be estimated in the cold and subsequently allowed for.

L. DE K.

Estimation of Nitrogen in Nitrates and Nitro-compounds by Kjeldahl's Method. By L. CHENEL (*Bull. Soc. Chim.* [3], 7, 321—327).—The author finds that Jodlbaur's modification of Kjeldahl's method for the determination of nitrogen (Abstr., 1886, 834) gives values agreeing closely with the theoretical with certain inorganic nitrates, methylamine nitrate, nitroglycerol, and several

nitro-derivatives of benzene; whilst, in the case of the nitro-naphthalenes, values corresponding only with 90 per cent. of the total nitrogen are obtained. The latter, however, gives good results, if the reduction is effected with phosphorus iodide instead of zinc dust. This is conveniently prepared by adding iodine (12 grams) to a solution of phosphorus (2 grams) in carbon bisulphide (15—20 c.c.), and evaporating to dryness on the water-bath. About 0.05 gram of the phosphorus iodide and 8 grams of water are added to a weighed quantity (0.5 gram) of the nitronaphthalene; concentrated sulphuric acid (25 c.c.) and mercury (0.7 gram) are introduced into the solution, and the remainder of the operation carried on as usual.

A. R. L.

Kjeldahl's Method of Estimating Nitrogen. By C. ARNOLD and K. WEDEMEYER (*Zeit. anal. Chem.*, **31**, 525—533).—Various suggestions have been made for expediting the oxidation of organic substances during the heating with sulphuric acid. The simultaneous adoption of Gunning's proposal to add potassium sulphate (*Abstr.*, 1889, 796) and that of Arnold to use both mercuric oxide and copper sulphate (*Abstr.*, 1887, 78) not only shortens materially the time required, but renders the method applicable to many substances, such as the azo-compounds, those containing the pyridine group, &c., which, with other modifications of the process, fail to yield all their nitrogen as ammonia. The proportions recommended are:—0.5 gram of substance, 30—50 grams of sulphuric acid, 15—30 grams of potassium sulphate, 1 gram of mercuric oxide, and 1 gram of cupric sulphate. To moderate the frothing which results from the presence of potassium sulphate, only half the proposed quantity is added at first, and the remainder after 10—15 minutes boiling. No potassium sulphate is needed if 2—3 grams of zinc powder is added instead of the usual fragments of zinc.

To render the method applicable to both organic and inorganic nitrates, benzoic or salicylic acid should be dissolved in the sulphuric acid (3 grams in 40 c.c.) before this is poured upon the substance. After mixing well, the acid is heated to boiling, the mercuric oxide and cupric sulphate are introduced, and, after 10—15 minutes longer boiling, the potassium sulphate.

M. J. S.

Estimation of Phosphoric Acid in Basic Slag. By A. F. JOLLES (*Zeit. anal. Chem.*, **31**, 516—519).—For dissolving basic slag for analysis, two methods have principally been in use, that namely with sulphuric acid and that with hydrochloric acid. It is now, however, established that the calcium sulphate obtained when sulphuric acid is used encloses and protects particles of calcium phosphate. The method of H. and E. Albert consists in boiling the slag with hydrochloric acid until the liquid is reduced to a few cubic centimetres of a thick jelly of silicic acid, at which stage they state that the addition of water will leave all the silica undissolved. This statement the author cannot confirm. He recommends the following modification:—5 grams of the powdered slag is moistened with water in a basin, boiled with 40 c.c. of 30 per cent. hydrochloric acid, evaporated completely to dryness, heated in an air-bath at 120°,

moistened with hydrochloric acid, dissolved in water, filtered, and made up to 500 c.c. Of this, 50 c.c. is mixed with 15 c.c. of Joulie's citrate solution (400 grams of citric acid made up to a litre with ammonia of sp. gr. 0.9), and precipitated as usual with magnesia mixture. The results obtained agree closely with those given by the molybdate method. Albert's suggestion to dissolve the washed ammonio-magnesium precipitate and titrate with uranium solution leads to higher numbers, in consequence, seemingly, of the slow development of the end indication with ferrocyanide. M. J. S.

Estimation of Phosphorus by neutralising the "Yellow Precipitate" with Alkali. By C. E. MANBY (*Chem. Centr.*, 1892, ii, 267; from *J. anal. Chem.*, 6, 82—85, 2).—In the analysis of steel and iron, the precipitate obtained with ammonium molybdate is dissolved in 15 per cent. ammonia and a little hot water, excess of ammonia is driven off by evaporation, 2 c.c. of nitric acid (sp. gr. 1.2) is added, the solution evaporated to dryness, and the residue ignited until all the ammonium nitrate has volatilised. The estimation is complete in 40 minutes. C. F. B.

Estimation of Sulphur in Slags. By J. TORREY (*Chem. Centr.*, 1892, ii, 265; from *J. anal. Chem.*, 6, 86).—Very concordant results were obtained by Craig's method, the hydrogen sulphide being absorbed in permanganate solution. The sulphur in pyrites may be determined by igniting in a stream of oxygen and absorbing the sulphurous anhydride formed in permanganate, the residue being washed with hot water, and the wash-water added to the permanganate before the sulphuric acid is precipitated. In some cases, it is advisable to add a little magnesium chloride to the hydrochloric acid in which the slag is to be dissolved. C. F. B.

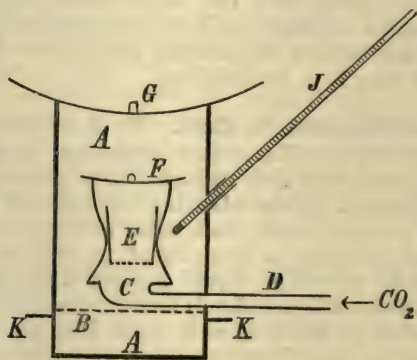
Estimation of Sulphur in Coal. By A. GRITNER (*Zeit. angew. Chem.*, 1892, 170—171).—The author estimates the total sulphur by Eschka's process, and from this deducts the sulphur contained in the ash. This is estimated by the following method:—1 gram of ash is moistened with bromine water, and, after adding 100 c.c. of hydrochloric acid, the mixture is evaporated on the water-bath until reduced to about 10 c.c. The liquid is then filtered, the insoluble matter being washed until completely free from sulphates; the filtrate is next concentrated to 100 c.c., and, while hot, precipitated with a slight excess of ammonia. The precipitate is washed on a filter with boiling water until all sulphate reaction has ceased; the filtrate is acidified with hydrochloric acid, and the sulphate estimated as usual. The test analyses are satisfactory. L. DE K.

Volumetric Estimation of Sulphuric Acid in Alkali Sulphates. By C. CHERIX (*Chem. Zeit.*, 16, 885).—The author proposes the following ingenious process:—Alkali sulphates are scarcely acted on by barium carbonate, but they are readily decomposed by barium hydroxide with formation of barium sulphate and caustic alkali. The unavoidable excess of barium is easily removed by a current of

carbonic anhydride, and the filtrate now contains alkali carbonate, which may be readily titrated in the usual manner by a standard acid and calculated into sulphuric acid. The presence of chlorides and nitrates does not in the least interfere. The two test analyses are very satisfactory.
L. DE K.

Estimation of Arsenious Anhydride. By A. BAUMANN (*Zeit. angew. Chem.*, 1892, 117).—The process is based on the fact that an alkaline solution of potassium ferricyanide is rapidly reduced by arsenious acid, and will consequently evolve less oxygen when mixed with hydrogen peroxide. The difference in oxygen evolved, before and after the addition of the arsenious acid, serves as a measure of the latter. 1 c.c. of oxygen corresponds with 4.425 milligrams of arsenious oxide.
L. DE K.

Estimation of Antimony and the Use of the Gooch Filter. By T. PAUL (*Zeit. anal. Chem.*, 31, 537—543).—Antimony is most conveniently and accurately weighed in the form of trisulphide, but as the precipitate usually contains an excess of sulphur, either free or as pentasulphide, it requires to be heated in an atmosphere of carbonic anhydride. For this operation the Gooch crucible (see *Chem. News*, 31, 181) presents several advantages. It allows the rapid filtration of large volumes of liquid, and the collection of either a large or small quantity of precipitate. For expelling the excess of sulphur, the author has constructed the apparatus here figured.



A is a cylindrical air bath with perforated false bottom B. CD is a glass tube, supporting the crucible E, and supplied with a stream of dry carbonic anhydride. F and G are glass covers through which the progress of the operation can be watched. Even when much sulphur is present, a temperature of 230°, maintained for an hour, suffices for its complete expulsion.
M. J. S.

Estimation of Antimonious Oxide. By A. BAUMANN (*Zeit. angew. Chem.*, 1892, 117—118).—Antimonious chloride behaves

towards an alkaline solution of potassium ferricyanide like arsenious anhydride, and may be estimated in an analogous manner (see preceding page). 1 c.c. of oxygen equals 6.4573 milligrams of antimonious oxide.

L. DE K.

Gas-volumetric Alkalimetry. By A. BAUMANN (*Zeit. angew. Chem.*, 1892, 114—116).—The process is based on the fact that a mixture of potassium ferricyanide and hydrogen peroxide does not evolve any oxygen unless free alkali is present. Very accurate results may be obtained, by using the author's apparatus, with the hydroxides of barium, calcium, potassium, and sodium, provided the two last are free from carbonic anhydride. The process is not suitable for taking the strength of ammonia. 1 c.c. of oxygen at N.T.P. = 5.0134 milligrams of potassium hydroxide, 3.5781 milligrams of sodium hydroxide, 6.0735 milligrams of barium hydroxide, and 3.30497 milligrams of calcium hydroxide. The solution of hydrogen peroxide should be perfectly free from acidity, and must, if necessary, be neutralised with calcium carbonate.

L. DE K.

Estimation of Free Alkali in Commercial Hypochlorites. By N. G. BLATTNER (*Chem. Zeit.*, 16, 885—886).—The author recommends one of the following three methods:—

1.—25 c.c. of the sample is mixed, in a 250 c.c. flask, with 50—100 c.c. of water, and then treated with an excess of ammonia, which decomposes the hypochlorite. The mixture is first gently heated, but is afterwards boiled down to a small bulk, so as to completely expel the excess of ammonia. After cooling, water is added to the mark, and the total alkalinity is now estimated in an aliquot part of the liquid by means of standard hydrochloric acid and methyl-orange. Another portion may be treated with solution of barium chloride, and the caustic alkali titrated with acid and phenolphthaleïn.

2.—10 c.c. of the sample is put into a 250 c.c. Erlenmeyer flask, and mixed with 150 c.c. of recently boiled, cold, distilled water and a few drops of a 1 per cent. alcoholic solution of phenolphthaleïn. If free alkali is present, the liquid will turn reddish, but on slowly adding standard acid, the colour will gradually disappear. The titration should be repeated, and it is as well to add another drop of phenolphthaleïn, when the reaction is finished, so as to make sure there is no more free alkali. The process, however, only gives the caustic alkali, whilst the first gives the alkali carbonate as well.

3.—Whilst engaged in investigating the action of metallic oxides on hypochlorites, the author thought of utilising the reaction between cobalt or nickel sesquioxide and a hypochlorite, by which the latter is reduced to chloride. Any free or carbonated alkali, may then be titrated with standard acid. To carry out the process, 25 c.c. of the sample is put into a 250 c.c. flask, diluted with water and first gently heated, but finally boiled, with a small quantity of precipitated cobalt or nickel sesquioxide. After cooling, water is added to the mark, and the alkali is estimated in the usual manner in 100 c.c. of the filtrate.

L. DE K.

Detection of Strontium in presence of Calcium. By K. P. MACELROY and W. D. BIGELOW (*Chem. Centr.*, 1892, ii, 424; from *J. Anal. Chem.*, 6, 26).—The mixed carbonates of calcium and strontium are dissolved in hydrochloric acid, the solution evaporated to dryness, and the residue extracted with a mixture of equal volumes of acetone and water. To the solution, a solution of potassium chromate in 50 per cent. acetone is added, when anhydrous strontium chromate is precipitated. If this is filtered off after 10 minutes, the filtrate contains no strontium, and only after several hours does calcium chromate crystallise out from it. C. F. B.

Qualitative Separation of the Barium Group. By A. GRITNER (*Zeit. angew. Chem.*, 1892, 73—74).—The author, who has made a large number of careful experiments, has found that although barium may be readily detected by adding a solution of calcium sulphate, the test is not very delicate in presence of calcium and strontium compounds, especially when large quantities of the former are present. But even very minute quantities of barium may be detected in presence of calcium and strontium by adding to the acetic solution a solution of potassium or ammonium chromate, and he therefore recommends this method of separation. L. DE K.

Schaffner's Volumetric Zinc Process. By E. PROST and V. HASSEIDTER (*Zeit. angew. Chem.*, 1892, 166—170).—This process, which is extensively used in France and Belgium, is briefly as follows:—2.5 grams of the zinc sulphide is treated with 12 c.c. of nitric acid, and then evaporated to dryness with excess of hydrochloric acid. The residue is moistened with 5 c.c. of hydrochloric acid, taken up with 50 c.c. of hot water, and treated with hydrogen sulphide. The precipitated sulphides are filtered off, and washed with a solution of hydrogen sulphide acidified with hydrochloric acid. The filtrate and washings are boiled to expel the hydrogen sulphide, and then again boiled with nitro-hydrochloric acid to oxidise any iron; after partial cooling, the liquid is introduced into a 500 c.c. flask, and mixed with 100 c.c. of ammonia and 10 c.c. of a saturated solution of ammonium carbonate. In the meantime, a standard zinc solution is prepared by dissolving about 1.5 grams of pure metallic zinc in a mixture of 20 c.c. of hydrochloric and 5 c.c. of nitric acid, and finally adding 300 c.c. of water, 100 c.c. of ammonia, and 10 c.c. of ammonium carbonate solution. After remaining over night, both liquids are made up to 500 c.c., and in 100 c.c. of the clear liquid, the zinc is estimated by means of sodium sulphide, using lead paper as indicator.

The authors have, however, found that the iron precipitate retains a not inconsiderable amount of zinc, and they therefore propose to add to the standard zinc solution approximately the same amount of ferric iron. Aluminium, if present, behaves like iron. Manganese must be got rid of by the addition of bromine water; hydrogen peroxide or sodium phosphate must not be used. The precipitated manganic oxide is free from zinc. Lead (if not previously removed by hydrogen sulphide) and calcium are completely removed by the ammonium

carbonate, and their carbonates are free from zinc. It is of the utmost importance to render the whole of the silica insoluble.

L. DE K.

Volumetric Estimation of Thallium. By E. SPONHOLZ (*Zeit. anal. Chem.*, **31**, 519—520).—Thallious salts are instantly oxidised to thallic compounds by bromine water, 1 atom of thallium requiring exactly 2 atoms of bromine. A N/6 solution is of convenient strength. The exact strength must be ascertained by means of iodide and thio-sulphate, and it is as well that this should be done with part of the contents of the burette which serves for the thallium titration, and as speedily as possible. The bromine is delivered into the acidified thallious solution from a burette whose jet dips into the solution, until an excess is indicated by the liquid becoming yellow. A correction is made for the amount of bromine required to colour the solution.

M. J. S.

Electrolytic Estimation of Copper. By G. P. DROSSBACH (*Chem. Zeit.*, **16**, 819).—Instead of using the usual acid solution, the author recommends electrolysing an ammoniacal solution of the copper. The precipitation proceeds more rapidly and the end reaction is more readily recognised; it also dispenses with the necessity of evaporating large quantities of free acid.

When using three middle-sized Meidinger cells, the author generally succeeded in finishing an analysis in about six hours. The current must, in every case, be stopped as soon as the last trace of copper has disappeared, otherwise other metals, such as nickel and zinc, may also come down. The process fails in presence of mercury and cadmium, and also of lead and silver, but these two are, of course, easily eliminated. Aluminium, arsenic, chromium, ferric iron, cobalt, nickel, zinc, tin, manganese, uranium, and bismuth do not sensibly interfere. The test analyses are remarkably accurate.

L. DE K.

Quantitative Analysis by Electrolysis. By F. RÜDORFF (*Zeit. angew. Chem.*, 1892, 3—7, 197—200).—The author uses by preference Meidinger's cells; if once properly filled and placed in a quiet spot, they keep in good working order for several months. As regards the strength of the current—8 cells give 2.6 c.c. of electrolytic gas per minute; 6 cells, 1.9 c.c.; 4 cells, 1.2 c.c.; 3 cells, 0.8 c.c.; and 2 cells, 0.02 c.c. of gas. The author's decomposition apparatus consists of a deep platinum dish, 60 mm. in height, 75 cm. in diameter, of about 40 grams in weight, and 170 c.c. capacity, and a stout platinum wire, one end of which is twisted like a spiral. Hemispherical dishes of 100—150 c.c. capacity answer the same purpose. As electrolytic precipitations take a rather long time, the author generally starts the analysis in the evening, when it will be completed early in the next morning. The author communicates what he considers to be improvements in the electrolytic separation of metals.

Copper.—The solution should not contain more than about 0.4 gram of the metal. Free acid should be neutralised with ammonia; 5 drops of nitric acid is then added, and the liquid made up to about 100 c.c. The electrolysis is effected by means of 2—6 cells, the basin being connected with the negative pole. When all the copper has

precipitated, the free nitric acid in the dish is rendered harmless by adding a little sodium acetate, the basin is disconnected, and the metallic copper washed, dried, and weighed. If the copper solution contains chlorides, the liquid is mixed with 3 grams of ammonium nitrate and 20 c.c. of ammonia, which, at the end of the operation, must be neutralised with acetic acid.

Mercury is estimated, like the copper, from an acid solution, or it may be precipitated from an ammoniacal solution after previously adding 0.5 gram of tartaric acid.

Silver.—The solution, which should contain about 0.3 gram of metal, is neutralised with sodium hydroxide and mixed with a slight excess of potassium cyanide. After diluting to about 100 c.c., the electrolysis is effected with the aid of 3–6 cells. The precipitated silver is thoroughly washed and dried at 100°.

Nickel.—The solution, which should contain about 0.3 gram of metal, is mixed with 25 c.c. of a saturated solution of ammonium sulphate and 25 c.c. of ammonia. After diluting to 100 c.c., the electrolysis is effected by means of 3–6 cells. Good results are also obtained by electrolysing an ammoniacal solution in presence of sodium pyrophosphate, using 4–6 cells. Chlorides should be absent.

Cobalt is estimated like nickel, using 6–8 cells.

Cadmium.—The solution, which should contain about 0.4 gram of metal, is, if necessary, neutralised, and mixed with excess of potassium cyanide. From 3 to 6 cells are used, and the precipitated metal is well washed with water, rinsed with alcohol, and dried at 80°, as at a higher temperature it is liable to oxidation.

Manganese.—The solution should, at most, contain 0.04 gram of manganese, which must be present as sulphate. After adding a few drops of dilute sulphuric acid and diluting to 100 c.c., the liquid is electrolysed by means of 2 cells. The manganese does not, however, separate as metal but as hydrated peroxide, which may be washed, dried at 60°, and weighed. Its weight multiplied by 0.523 equals the metallic manganese.

Zinc.—The solution, which should contain about 0.2 gram of metal, is mixed with 20 c.c. of a 25 per cent. solution of sodium acetate and 3 drops of acetic acid. 5–6 cells are used for the electrolysis, which is carried on in a platinum dish previously coated inside with metallic copper. The zinc solution should be free from nitrates or chlorides.

Iron.—The solution, which should contain about 0.3 gram of metal, is, if necessary, neutralised with ammonia and mixed with 60 c.c. of a saturated solution of ammonium oxalate. After diluting to 120 c.c., the metal is precipitated by means of 6–8 cells, and, after washing, dried at 100°, and weighed.

Lead.—The solution, which should contain about 0.1 gram of metal, is mixed with a few c.c. of nitric acid and 10 c.c. of a solution of copper nitrate containing 1 per cent. of metallic copper. The dish is connected with the positive pole and 3–4 cells are used, which cause the lead to precipitate, not as metal, but as peroxide, which may, after washing and drying at 120°, be weighed as such.

Tin.—The solution, which should not contain more than 0.3 gram of metal, is neutralised with ammonia and mixed with 30 c.c. of a

cold saturated solution of ammonium hydrogen oxalate. 3—6 cells are used, and the precipitated metal is finally dried at 80° and weighed. If the tin solution should be turbid, it must be cleared by gentle heating.

Bismuth.—The solution, which should contain not more than 0.1 gram of metal and but little free nitric acid, is mixed with but slight excess of strong solution of sodium pyrophosphate, then with 20 c.c. of a saturated solution of potassium oxalate and sulphate, and finally made up to 120 c.c. After exposing it to the action of 4 cells for about 20 hours, the precipitation of the bismuth will be found to be complete. After washing and drying at 60°, it may be weighed.

Antimony.—The solution, which should contain about 0.15 gram of metal, is mixed with 30 c.c. of a 10 per cent. solution of sodium monosulphide and electrolysed by means of 2—3 cells. The metal must be cautiously washed with water and dried at 60°. The author does not give any test analyses, but he invites analysts to try his processes and convince themselves of their usefulness.

L. DE K.

Separation and Estimation of Tin, Antimony, Lead, and Copper in Alloys. By M. SCHMIDT and H. DREYER (*Chem. Zeit.*, 16, 696).—About 1 gram of the finely-divided sample is fused in a porcelain crucible with 3 grams of dry sodium carbonate and 3 grams of sulphur for 20 minutes, to convert the metals into sulphides. The mass is extracted with water, and the insoluble matter collected and washed with a hot solution of sodium sulphide. The filter is then put into a beaker, heated with nitric acid to dissolve the sulphides of lead and copper, and the solution filtered and evaporated with sulphuric acid to separate the lead as sulphate. After washing this with dilute alcohol, the copper is precipitated by means of pure metallic zinc.

The alkaline filtrate is first acidified with hydrochloric acid and then heated on the water-bath with excess of the acid to redissolve the sulphides of antimony and tin. After filtering off from the sulphur, the liquid is heated for two or three hours with iron wire to precipitate the antimony. This is then washed with alcohol and weighed. As it may contain traces of copper, it must be treated with nitric acid and the copper estimated colorimetrically. The filtrate from the antimony, which now contains the tin, is diluted with water and treated with hydrogen sulphide. After the precipitate has completely subsided, it is collected, washed, and converted in the well-known manner into stannic oxide, which is then weighed.

The authors got very satisfactory results with this process, their analyses generally coming up to 99.7°.

L. DE K.

Precipitation of Aluminium in presence of Lithium. By K. SPONHOLZ and E. SPONHOLZ (*Zeit. anal. Chem.*, 31, 521—522).—The separation of lithium from aluminium by precipitation with ammonia from sulphate solutions is not complete with less than five precipitations. With ammonium acetate, one, or, at most, two, precipitations are sufficient. The dilute solution mixed with ammonium acetate is heated for a short time on the water-bath, adding during the heating

enough ammonia to keep the acidity low. The precipitate is transferred completely to a filter without suction, and is then washed by suction with hot water containing ammonium acetate until the spectroscope shows no lithium in the washings. It is immaterial whether the original solution contained sulphates or chlorides, and the presence of alkalis and alkaline earths does not affect the accuracy of the separation.

M. J. S.

Estimation of Aluminium in Ferroaluminium. By E. DONATH (*Zeit. angew. Chem.*, 1892, 13).—Regelsberger (this vol., ii, 48) has made use of potassium cyanide to prevent the precipitation of iron when throwing down the aluminium. The author claims to have investigated a similar process in 1880, and to have made use of sodium thiosulphate for the reduction of the ferric iron. Regelsberger's reducing agents, sodium hydrogen sulphite or iron wire, are less convenient, the former acting too slowly, and the latter unnecessarily increasing the amount of iron. The cyanide process may, however, be greatly improved by a preliminary precipitation of the alumina, care being taken that as little as possible of the iron is coprecipitated.

L. DE K.

Analysis of Ferrochrome, Ferroaluminium, Ferrotungsten, Ferrosilicon, and Ferrotitanium. By A. ZIEGLER (*Zeit. anal. Chem.*, 31, 558—563; from *Dingl. polyt. J.*, 279, 163).—With the exception of ferrotitanium, these alloys are best attacked by fusing the finely powdered substance with a mixture of 12 parts of alkali hydroxide and 6 parts of nitrate for half an hour in a silver crucible. To minimise the action on the crucible, it is advisable to heat with the small, smoky flame of a Bunsen's burner of which the air holes are nearly closed. The melt is boiled out with water; then, if chromium is present, the solution is treated for half an hour with carbonic anhydride, evaporated to dryness on the water-bath, redissolved, and filtered, washing with dilute sodium carbonate. In the filtrate, silica and chromium are estimated. The residue is dissolved from the filter with hydrochloric acid, and in the solution silica, manganese, and iron are estimated.

For estimation of the phosphorus, the fused mass is dissolved in nitric acid with a little hydrochloric acid, and then, by repeated evaporation with strong nitric acid, the hydrochloric acid is expelled before neutralising with ammonia and precipitating the phosphoric acid as usual.

Ferroaluminium requires a longer fusion than ferrochrome; the treatment of the solution with carbonic anhydride and the evaporation are in this case to be omitted. Another method is to dissolve the alloy in hydrochloric acid and evaporate the solution to dryness, adding nitric acid to oxidise the ferrous chloride, then transfer the residue to the silver crucible, and fuse with the mixture of alkali and nitrate.

Ferrosilicon may also be attacked by fusing with sodium hydrogen sulphate, if it is certain that no silicon hydride is formed. By avoiding a high temperature during the fusion, the metallic sulphates may be completely brought into solution when the fused mass is digested with hot water acidified with sulphuric acid.

Ferrotitanium can only be dissolved by fusion with sodium hydrogen sulphate and treatment with cold water. The filtrate from the silica is diluted to a litre, neutralised with ammonia, mixed with aqueous sulphurous acid, and boiled for two hours. The precipitate of impure metatitanic acid is fused again with bisulphate, and again precipitated as before, when a pure, white precipitate should be obtained. The filtrates should again be neutralised, reduced, and re-boiled to ensure that precipitation has been complete.

In all cases the completeness of the attack and the purity of the precipitates must be confirmed. M. J. S.

Electrolytic Separation of Platinum and Palladium from Iridium. By E. F. SMITH (*Amer. Chem. J.*, **14**, 435—437).—The combined influence of an alkali phosphate and phosphoric acid entirely prevents the electrolytic deposition of iridium from its solutions, but does not hinder that of palladium or platinum, so that either of the latter metals may be estimated by this means in the presence of the former. The metal is most conveniently deposited on a cathode consisting of a silver-plated platinum dish (see *Abstr.*, 1890, 831). It is always bright and firmly adherent, and should be washed with hot water before being dried and weighed. If copper is substituted for the silver lining, a further washing with alcohol is necessary to avoid oxidation of the copper whilst drying; but this is objectionable, as the alcohol tends to loosen the deposit. The proportions to be observed, and the degree of accuracy to be expected, will be seen from the following trial experiments:—A solution (200 c.c.) containing palladium (0.1458 gram), iridium (0.1200 gram), hydrogen disodium phosphate (40 c.c. aqueous, sp. gr. 1.0358), and phosphoric acid (5 c.c. aqueous, sp. gr. 1.47) was subjected for a night to a current capable of liberating 2 c.c. of electrolytic gas per minute; the increase of weight of the silvered platinum dish was 0.1449 gram. Another solution (270 c.c.) containing platinum (0.1042 gram), iridium, phosphate, and phosphoric acid as before, was subjected for the same time to a current giving 1.8 c.c. of electrolytic gas per minute; the increase in weight of the dish was 0.1048 gram. Although the metal rhodium is completely deposited from its solutions under the above conditions, experiments made with the view of separating it from iridium did not prove satisfactory. J. N. W.

Estimation of Clay and Sand in Soils. By F. TSCHAPLOWITZ (*Zeit. anal. Chem.*, **31**, 487—501).—In the mechanical analysis of soils, it has been usual to regard as clay that portion which can be removed by elutriation under certain specified conditions. Calculated from the formula which, according to Schöne, connects the diameter, d , of a particle of clay with the velocity, v , with which it falls through water, $d = v^{\frac{1}{2}} 0.0314$ mm., the upper limit of the diameter of the particles regarded as clay by Schlösing is 0.0005 mm.; by Mayer, 0.028 mm.; by Wolff and Knop, 0.01 mm.; by Orth and Laufer, 0.05 mm. The author's own experiments show that the majority of the particles in an ordinary clay have a diameter less than 0.006 mm., whilst those between 0.01 and 0.05 mm. are, at

least in some cases, nothing but crystalline sand. He therefore proposes that 0.01 mm. should be conventionally adopted as the superior limit, and recommends the following mode of procedure:—From 5 to 15 grams of the air-dried soil is boiled with 5 to 6 parts of water until all lumps are broken up. Sufficient 10 per cent. hydrochloric acid is then added to dissolve all carbonates, then more water and acid until the whole measures about 100 c.c. and contains 10 per cent. of free acid. It is again boiled and allowed to deposit for 24 hours. The turbid liquid is poured off and the sediment twice washed with warm water by decantation. The washed soil is next heated, but not boiled, with about 100 c.c. of 3 per cent. ammonia to dissolve humus, and washed as before. The turbid acid and alkaline washings are allowed to deposit completely, and the sediments from them are ignited and included in the clay result. The purified soil is next washed through a sieve of 0.1 mm. mesh, and the coarse particles are ignited and weighed. The liquid which has passed through the sieve is allowed to deposit for 24 hours or longer, the upper liquid is siphoned off, and if turbid is allowed further to settle. The purified soil is now submitted to the following process ("Aufschichtensmethode") :—A cylinder of 8 cm. diameter and 25 cm. (?) high is filled to a height of 20 cm. with distilled water. Upon the surface of this, by means of a funnel, the tube of which is bent at a right angle, the soil, suspended in 80—100 c.c. of water, is carefully delivered, 100 c.c. of water being further used for rinsing. After 20 minutes, the time required by Schöne's formula for particles larger than 0.01 mm. to subside, the liquid is drawn off by a siphon whose shorter leg is turned up for 2 cm. The residue is similarly treated as long as the water siphoned off is not clear. The portions of liquid siphoned off are warmed, and if they fail to settle clear they are evaporated to dryness, dried at 150°, or ignited and recorded as clay. The coarser sediment, together with that taken out by the sieve, constitutes the sand.

To determine the capacity of a soil for absorption of water, about 5 grams is weighed in a small, deep porcelain basin, with which a rounded glass rod has been tared. Water is then gradually added whilst the mixture is stirred to the utmost attainable uniformity. The stage of incipient fluidity, or that at which a furrow drawn with the rod begins instantly to fill up but does not disappear for a second or two, is easily determined to within three or four drops of water. It is well to overpass this stage, and then return to it by partially drying the paste and repeating the process. The weight of the water present is then ascertained. The absorptive power of a clay depends mainly on the average size of its particles, and is closely connected with its plasticity.

M. J. S.

Gas-volumetric Estimation of Potassium Ferricyanide. By A. BAUMANN (*Zeit. angew. Chem.*, 1892, 113—114).—Potassium ferricyanide is readily tested as to its purity in the author's apparatus (compare Abstr., 1892, 103). The sample, dissolved in a small quantity of water, is introduced into the outer chamber of the generating vessel, and mixed with 5 c.c. of a solution of potassium hydroxide. From 5 to 10 c.c. of 2 per cent. hydrogen peroxide is put into the

annexed glass cylinder, and after the apparatus has been surrounded by cold water for some time, the operation is conducted as described in the former paper. 1 c.c. of liberated oxygen at N.T.P. corresponds with 0.029447 gram of potassium ferricyanide.

L. DE K.

Ammonium Magnesium Urate. By G. GUÉRIN and H. THORION (*J. Pharm.* [5], 26, 202—204).—This salt, $(C_5H_2N_4O_3H)_{10}(NH_4)_2Mg + 45H_2O$, is easily obtained by precipitation. On adding magnesium solution to urine, the precipitate contains the whole of the uric acid as well as the phosphoric acid; hence the pyrophosphate resulting from ignition of the precipitate always contains an excess of magnesia, corresponding with the amount of uric acid present in the urine. J. T.

Estimation of a Mixture of Saccharose, Dextrose, and Levulose. By F. G. WIECHMANN (*Chem. News*, 66, 237—239; 249—251).—The method to be described involves three analytical operations: two gravimetric determinations and one optical examination with the polariscope. Of course, the process is to be applied only in cases where no other optically active substance is present.

An amount of the sample equal to 10 grams of dry substance is weighed out, placed in an accurately graduated 100 c.c. flask, dissolved in water, and finally made up to the mark with distilled water.

Optical Examination.—Some of the solution is placed in a water-jacketed polarisation tube, provided with a thermometer, and a reading of the solution is taken in the polariscope at 20°. The reading thus obtained must be reduced to the basis of one made in a 100 mm.-tube, and, if a sugar scale has been used for the observation, the reading must be transformed into circular degrees. With a polariscope using 26.048 grams as the normal weight, the factor 0.346 is used for the sodium ray.

Gravimetric Estimation before Inversion.—10 c.c. of the solution (= 1 gram of dry substance) is made up to 150 c.c., and of this 24.4 c.c. (= 0.1628 gram of dry substance) is taken. 50 c.c. of Fehling solution is heated to boiling, the sugar solution is added and the mixture boiled for three minutes. After diluting the mixture with cold water, previously boiled, the cuprous oxide is collected on a weighed asbestos filter, and washed, first with boiling water, then with absolute alcohol, and finally with ether. The weighed precipitate is calculated to its equivalent of metallic copper, and from this figure the corresponding amount of saccharose can be ascertained. The total reducing sugars are calculated by adding 1/20 to the saccharose value indicated.

Gravimetric Estimation after Inversion.—50 c.c. (= 5 grams of dry substance) is heated on the water-bath with 4 c.c. of hydrochloric acid, sp. gr. 1.20, for five minutes at 67°. The flask is then removed, and after cooling to the original temperature, the contents are made up to exactly 100 c.c. Of this solution 20 c.c. is neutralised exactly with sodium carbonate, and made up to 150 c.c.; of this solution 24.4 c.c. (= 0.1628 gram of dry substance) is taken and treated with the alkaline copper solution as directed. The result expresses the total sugars as saccharose. If now the previously found saccharose value

is deducted, the difference will represent the actual amount of cane sugar.

As the specific rotatory powers of saccharose, dextrose, and levulose are accurately known, the operator will now be in possession of all the *data* required for an algebraic calculation of their percentages.

The test-analyses are highly satisfactory. The saccharose used in the experiments was made from the purest granulated sugar by repeated washing with absolute alcohol. The dextrose was prepared from commercial anhydrous dextrose by treatment with best blood carbon and repeated crystallisation from absolute alcohol. The levulose was prepared by inverting inulin with very dilute hydrochloric acid, and twice crystallising the product from absolute alcohol. It was then tested both optically and chemically, and found to be pure.

L. DE K.

Estimation of Sugar in Cocoa Preparations. By M. SCHROEDER (*Zeit. angew. Chem.*, 1892, 173—183).—The author, who has conducted a large number of experiments, states that the detection and estimation of grape sugar in mixed cocoas or chocolates cannot be effected by Fehling's solution in the presence of cane sugar, as most commercial sugar contains a little invert sugar, which also gives reduction. Good results may, however, be obtained by using the polariscope as, when grape sugar is present, the rotation, after inversion, will be considerably less than it should be. By way of a check, the solution may be subjected to fermentation. Commercial grape sugar invariably contains amylin, which, not being fermentable, may afterwards be readily recognised both by optical and chemical tests.

L. DE K.

Pentoses in Urine. By E. SALKOWSKI (*Chem. Centr.*, 1892, ii, 483; from *Centr. med. Wiss.*, 1892, 593—595).—Pentoses, possibly xylose, certainly occur at times in urine. To detect them, a little phloroglucinol is dissolved in warm hydrochloric acid, a slight excess of the former being taken; the solution is divided into two equal parts: to one, 0.5 c.c. of the urine to be examined is added, to the other an equal volume of normal urine of about the same concentration. The latter hardly changes in colour, but the former, if pentoses are present, becomes red at the surface, and the red colour gradually extends down into the liquid; this red colouring matter is dissolved on shaking with amyl alcohol. 0.5 per cent. of arabinose can be very easily detected by this method; 0.1 is recognised only with difficulty.

C. F. B.

Volumetric Estimation of Phenol in Urine. By A. KOSSLER and E. PENNY (*Zeit. physiol. Chem.*, 17, 117—139).—The two volumetric methods of estimating phenol are those of Koppeschaar (*Zeit. anal. Chem.*, 15, 233) and of Messinger and Vortmann (*Ber.*, 22, 2313).

Koppeschaar's method consists in adding an excess of a mixture of alkali bromide and bromate (in the proportion of 5 mols. to 1), and acidifying with hydrochloric acid, when bromine is liberated; potassium iodide is then added, and the iodine set free is estimated with thiosulphate, the deficiency in the amount of the bromine liberated indicating the amount of phenol present.

Messinger and Vortmann dissolve 2—3 grams of phenol in soda, so that there are at least 3 mols. of soda to one of phenol. The solution is diluted to 250—500 c.c., warmed to 60°, and decinormal iodine solution added in excess. After cooling, dilute sulphuric acid is added, and the excess of iodine estimated with sodium thiosulphate. 6 atoms of the iodine, which has been used up, correspond with one of phenol.

Koppeschaar's method gives good results, but is not so accurate as Messinger and Vortmann's for small quantities of cresol. The latter method gives good results with both phenol and cresol. In estimating phenol, it is necessary in order that it may be wholly transformed into tri-iodophenol, that there should be present somewhat over 3 mols. of sodium hypiodite to one of phenol, and that free iodine (5 c.c. of decinormal solution) should be present.

In estimating cresol, constant results are obtained if to each molecule more than seven of hypiodite, and at least 15 c.c. of decinormal iodine solution, are present.

Applied to urine, these methods give higher results than the methods previously adopted. In the 24 hours urine, as much as 0.07, and in one case 0.106 gram of phenol was present.

W. D. H.

Estimation of Uric Acid in Urine by the Haycraft-Herrmann Method. By E. DEROIDE (*Bull. Soc. Chim.* [3], 7, 363—364).—The high results obtained with the Haycraft-Herrmann method of estimating uric acid in urine, which depends on the volumetric determination of the silver in the precipitate of silver urate, are not due to the want of constancy in composition of this precipitate, but to the simultaneous precipitation of silver compounds of the xanthine group insoluble in ammonia.

A. R. L.

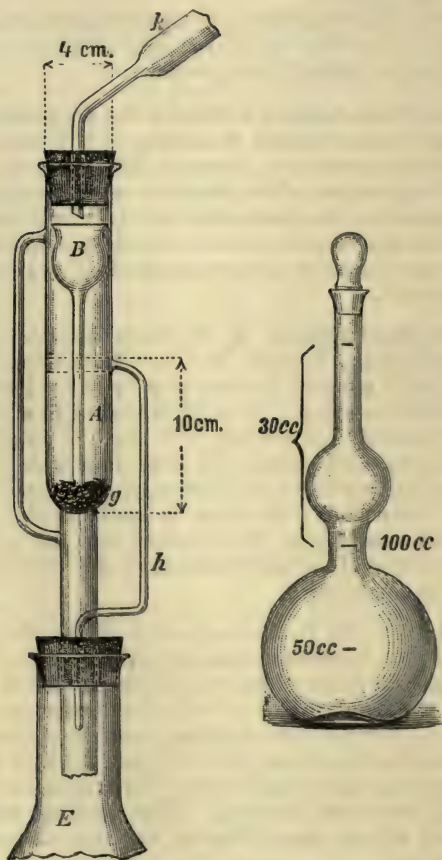
Estimation of Fat in Milk. By W. THÖRNER (*Chem. Centr.*, 1892, ii, 429; from *Molk. Zeit.*, 2, 1892, No. 1).—The following rapid and exact method is to be adopted in Germany by the police officials, and is described in detail:—10 c.c. of milk is placed in a tube of special shape, and saponified by adding 1.5 c.c. of alcoholic potash (16 grams per litre), and placing the tube in a water-bath for two minutes. 1 c.c. of strong acetic, sulphuric, or other acid is then added, to separate the fatty acids; the tube is again heated, then centrifugalised for 1—4 minutes at 2000 revolutions per minute, heated to 100°, and the volume of the fatty acids read off. For further details the paper must be consulted.

C. F. B.

Analysis of Lard. By C. AMTHOR and J. ZINK (*Zeit. anal. Chem.*, 31, 534—537).—This communication gives the results of the examination, by recognised methods, of three samples of lard rendered in the laboratory from the fat of different individual pigs, and at different times of the year. They exhibit nothing remarkable, except that the iodine absorption was low, being 50—52.6 per cent. in the fresh lard and slightly decreasing with age; that of the fatty acids (51.6—52.27) diminished even more on keeping. The melting and solidifying points of the fat altered but little on keeping; those of the fatty acids rose somewhat.

In estimating the iodine absorption, it is immaterial whether a large or a small excess of iodine be added, but an old iodine solution gives more concordant results than a new one. M. J. S.

Analysis of Mixtures of Saponifiable and Unsaponifiable Fats. By M. HÖNIG and G. SPITZ (*Zeit. angew. Chem.*, 1891, 565—568). —The two processes chiefly employed are very unsatisfactory, and have caused many complaints. An exception must, however, be made in favour of a method recommended by Morawsky and Dembsky, which consists in shaking out the soap solution with light petroleum. With care, this process gives not only concordant but also absolutely trustworthy results. The authors, who have thoroughly investigated the process, now operate as follows:—7 to 10 grams of the sample is boiled in a reflux apparatus with 20—25 c.c. of alcoholic potash and the same volume of alcohol for about two minutes. 30—40 c.c. of



water is added, and the boiling repeated. After cooling, the soap solution is transferred to a separating funnel, and the flask rinsed, first with a little 50 per cent. alcohol, and then with 50 c.c. of light petroleum. The whole is now thoroughly shaken, and then allowed to remain at rest. The petroleum soon separates cleanly from the soap solution. The latter is drawn off, and the petroleum is washed a few times with 10 to 15 c.c. of weak alcohol, the washings being added to the main liquid. The soap solution must now again be shaken out with fresh petroleum until this, on evaporation on filter paper, yields no fatty residue. The petroleum washings, after being in turn washed with alcohol, are added to the main liquid, which is then distilled off. The residue, consisting of the unsaponifiable fat, is then weighed.

If a great many estimations have to be performed, the quickest way is to extract the soap solution in one operation, for which the authors have devised the following Soxhlet-like apparatus (see illustration). The soap solution, which should not exceed 50 c.c. in bulk, is put into the container *A*, in which has been previously introduced a layer of small glass beads, *g*, 1 cm. deep. The surface of the soap solution should reach up to about 5 mm. from the mouth of the drawing-off tube *h*. The funnel-shaped tube *B* (the upper part of a thistle funnel) is now put in its place, the apparatus connected with the extraction-flask *E*, and another 20 c.c. of light petroleum is added. The whole apparatus is then connected with a reflux condenser, and the petroleum is boiled until the soap solution seems quite clear, and the petroleum which runs off is quite colourless. As a little soap also dissolves, this must be removed by finally agitating the petroleum a few times with 50 per cent. alcohol.

If, for technical purposes, only an approximate estimation is required, the authors use a 100 c.c. flask (see figure), which also has a 50 c.c. mark. The neck is marked off in 30 c.c.

2 or 3 grams of the sample is put into the dry flask, and saponified with alcoholic potash. Alcohol is added up to the 50 c.c. mark, and then water up to the 100 c.c. mark. Light petroleum (boiling point 50—70°) is then added up to the top mark, and the whole is well shaken. After complete separation has taken place, an aliquot part of the top layer is pipetted off and evaporated, and the residual fatty matter is weighed.

L. DE K.

Hübl's Iodine Numbers. By W. FAHRION (*Chem. Zeit.*, 16, 862—863).—The author has finally adopted the following process:—About 0.15 gram of any fat or oil is dissolved in 10 c.c. of pure chloroform and mixed first with 10 c.c. of a 6 per cent. alcoholic solution of mercuric chloride, and then with 10 c.c. of a 5 per cent. alcoholic solution of iodine. After two hours, 20 c.c. of a 10 per cent. solution of potassium iodide is added, the liquid diluted to 150 c.c. with water, and then titrated with N/10 sodium thiosulphate, but without addition of starch. A blank experiment must, of course, be made, and, if the analysis is to be trusted, the check must take at least twice the amount of thiosulphate required by the fatty mixture.

L. DE K.

Analysis of Mixtures of Ammonia and Methylamines. By H. QUANTIN (*Compt. rend.*, 115, 561—562).—The impure methylamines are distilled with milk of lime, and the distillate is collected in pure water, which is then digested with sufficient freshly precipitated magnesium phosphate to convert all the bases, calculated as ammonia, into ammonium magnesium phosphate. The methylamine present maintains the necessary alkalinity, and the precipitation of the ammonia is practically complete, but if the liquid is poor in methylamine, a second treatment with magnesium phosphate may be necessary. The liquid when distilled yields the methylamines free from ammonia.

In order to make a quantitative analysis, the total alkalinity of the volatile bases is determined. The ammonia is then precipitated by sodium phosphate and magnesium sulphate in presence of methylamines, and the ammonia in the precipitate is estimated. The methylamines are converted into platinochlorides, and the trimethylamine salt is removed by washing with alcohol. The weight of the mixed platinochlorides of methylamine and dimethylamine, together with the weight of platinum left on ignition, enables the quantities of the two bases to be calculated. The trimethylamine is estimated from the total alkalinity by difference.

C. H. B.

Estimation of Peptone by Precipitation as Mercury Peptonate. By L. A. HALLOPEAU (*Compt. rend.*, 115, 356—358).—The neutral or very slightly acid solution of peptone, free from other proteïds, is mixed with its own volume of a solution of mercuric nitrate, and allowed to remain for 18 to 24 hours. The precipitate is then washed with cold water until free from excess of mercury, collected on a tared filter, and dried at 106—108°; the weight when multiplied by the coefficient 0.666 gives the weight of peptone.

The mercuric nitrate solution is prepared by heating 100 to 150 grams of pure commercial mercuric nitrate with a litre of water for 15 to 20 minutes. The liquid is filtered, heated nearly to boiling, mixed with sodium carbonate solution, drop by drop, with agitation, until a slight permanent precipitate is formed, again filtered, and diluted to one litre.

Chlorides, in the proportion in which they are present in commercial peptones or the gastric juices, do not affect the estimation, provided that a sufficient quantity of mercuric nitrate is added.

In order to remove other proteïds, the solution (supposed to be acid with hydrochloric acid) is exactly neutralised with sodium carbonate; syntonin is precipitated. The filtrate, faintly acidified with acetic acid, is heated on a water-bath for half an hour; albumin separates as a flocculent precipitate. The filtrate from the albumin is mixed with nitric acid drop by drop, until a permanent precipitate forms, and the liquid is agitated and allowed to remain until the hemialbumose separates. It is filtered off, and washed with a small quantity of water slightly acidified with nitric acid; the filtrate contains the peptone, and after being carefully neutralised with sodium carbonate, is treated in the manner described above.

C. H. B.

General and Physical Chemistry.

Rotatory Power of Salts of the Diamines. By A. COLSON (*Compt. rend.*, 115, 729—732; and C. FRIEDEL, *ibid.*, 763—764).—Colson finds that when diacetyltartaric acid is saturated with ethylenediamine it yields a normal salt, which is very soluble in water but will not crystallise from it. A solution of 2.3 grams of the salt in 20 c.c. of water, in a column 200 mm. long, had a lævorotatory power of $-2^{\circ} 56'$. The acid salt is soluble in water and crystallises in long prisms; a solution of the same strength as the normal salt, and under the same conditions, has a lævorotatory power of $-3^{\circ} 55'$.

Normal ethylenediamine tartrate crystallises in lamellæ which are very soluble in water. 20 c.c. of an aqueous solution containing a quantity of salt equivalent to 1.2 grams of tartaric acid, in a column 200 mm. long, has a rotatory power of $+4^{\circ} 54'$. A solution of only one-fourth the strength gave almost exactly one-fourth of the rotation, and hence it would seem that the dissociation of the salt by water takes place to a very slight extent. Ethylenediamine hydrogen tartrate is much less soluble in water, but the solution is distinctly dextrogyrate.

It will be seen that the rotatory power of all these salts is of the same sign as that of the acid from which they are derived. Most of them are exceptions to the rules laid down by Guye. Diacetyltartaric acid is lævorotatory, but its anhydride is dextrorotatory, and this difference is due, according to Guye and Le Bel, to the occurrence of a closed chain $(CO)_2O$, which alters the positions of the atoms H, C, C, H, but Colson finds that the normal salt of ethylenediamine, which also contains a closed chain, is lævogryate, like the acid, and not dextrogyrate, like the anhydride. The hydrogen salt, according to Guye's views, should be dextrogyrate, but is, as a matter of fact, lævogryate.

The author attaches great importance to what he terms the *conservation of the molecular type*. Whenever, without any profound alteration of its constitution, an optically active compound gives rise, directly, to a series of compounds, or inversely, it communicates to the latter its optical properties. All the tartrates are optically active, because they are derived from an active original, which they can regenerate, the dissymmetrical type of the tartaric acid being preserved in its derivatives.

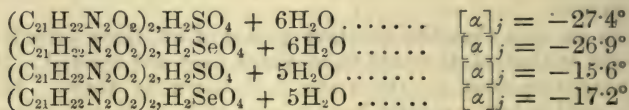
In accordance with the same principle, an inactive acid cannot produce active salts, a conclusion which is, however, in contradiction to the theory of asymmetric carbon. This conception, which is unable to explain the formation of racemates, predicts, on the other hand, that certain citrates, tartronates, isosuccinates, glyceroxides, &c., possess optical activity, although glycerol, citric and tartronic acids, &c., are inactive.

Friedel points out that Colson attributes to Guye a statement which is quite contrary to the principles of stereochemistry, namely,

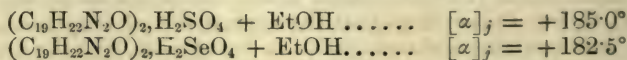
that in active tartaric acid the four atoms H, C, C, H are in the same plane. This might be the case in the inactive acid, but in the optically active acid, which according to the predictions of Pasteur, and also according to stereochemical theory, has no plane of symmetry, the four atoms are not in the same plane, much less in a plane of symmetry. Moreover, the plane which Colson regards as the plane of symmetry is not a plane of symmetry in inactive tartaric acid, but is perpendicular to the only plane of symmetry existing in a molecule built up from representative tetrahedra. C. H. B.

Rotatory Power of Salts of Diamines. By A. COLSON (*Compt. rend.*, 115, 948—950).—A rejoinder to Friedel (preceding abstract).

Rotatory Power of Solutions. By G. WYROUBOFF (*Compt. rend.*, 115, 832—834).—Solutions of strychnine have a levorotatory power $[\alpha]_j = -132$, whilst solutions of strychnine sulphate have a rotatory power of only $[\alpha]_j = -30.5^\circ$. If this difference is due to the weighting of one side of the molecule by the sulphuric acid molecule, it follows that the rotatory power of strychnine selenate should be less. The rotatory powers of the two hydrates of strychnine selenate and strychnine sulphate, which are respectively isomorphous, are as follows:—

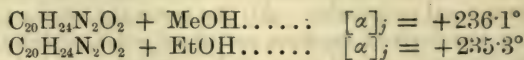


Similar relations are observed in the case of cinchonine:—



the rotatory power of the cinchonine being $+234^\circ$.

The rotatory power of anhydrous quinidine in solution in ethyl alcohol is $[\alpha]_j = +268.6^\circ$, whilst in methyl alcohol it is $+257.5^\circ$. The difference is due to the fact that quinidine crystallises with one molecule of each of these alcohols, and the crystals are isomorphous.



Compounds geometrically and optically isomorphous have, in solution, specific rotatory powers which are practically identical.

The rotatory power of dissolved compounds, like the rotatory power of crystals, is a phenomenon of the nature of reticulation, which depends on the symmetry peculiar to the crystalline grating. Particles retain this symmetry in solution, and as the symmetry depends not only on the chemical molecule, but also on the water of crystallisation (or whatever is playing the same part), it follows that there is no dissociation in solution, much less a separation into ions.

C. H. B.

Transformation of Electrical into Chemical Energy. By L. MILLER (*Zeit. physikal. Chem.*, **10**, 459—466).—Gore (*Abstr.*, 1892, 254), Regnault, and others have maintained that there is a *sudden* change in the electromotive force of a galvanic element when the metal or alloy forming one of the electrodes passes through its fusing point. The author shows that this is theoretically impossible, leading to a contradiction of the second law of thermodynamics. He has also attacked the problem from the experimental side. A large test-tube was made to contain a galvanic element consisting of a suitable electrolyte and two metals, one of which could be fused below the highest temperature of experiment. The fusible metal was melted into the very short wide limb of a U-tube, the other limb being long and capillary. Contact was made by means of a platinum wire passing down the capillary tube. The bulb of the thermometer employed was dipped into the fused metal, which was then allowed to solidify. The difference of potential of the two metals was ascertained by means of a capillary electrometer, the error of experiment being about 0.001 volt. The temperature of the element was gradually raised, and the E.M.F. read off at every degree in the neighbourhood of the melting point of the metal. The combinations used were lead and silver in fused potassium and zinc chlorides, mercury and amalgamated cadmium in 50 per cent. sulphuric acid, and tin and silver in a fused mixture of the nitrates of potassium, sodium, and calcium. No sudden jump in the value of the E.M.F. was observed at the melting points of the lead, mercury, and tin. Accurate experiments with alloys are difficult to make on account of chemical changes at their surfaces. J. W.

The Clark Cell as a Standard of Electromotive Force. By R. T. GLAZEBROOK and S. SKINNER (*Proc. Roy. Soc.*, **51**, 60—67).—The authors have determined the absolute electromotive force of a Clark cell, prepared by Lord Rayleigh in 1883, in terms of a known resistance and the electrochemical equivalent of silver. The resistance (about 1 B.A. unit) was a strip of platinoid immersed in a bath of paraffin oil, and the current employed varied from 0.75 to 1.4 ampères. On the assumption that 1 B.A. unit is equal to 0.9866 ohm, that the quantity of silver deposited by 1 ampère in 1 second is 0.001118 gram, and that the temperature coefficient of the E.M.F. is 0.00076, the E.M.F. of the cell at 15° was found to be 1.4342 volts, or 1.4324 volts at 12° F.

A large number of cells constructed at different times by Lord Rayleigh and others were examined, and very little difference was found between the electromotive forces, the variations from the standard being rarely greater than 0.0005 volt. Cells prepared in accordance with the provisional memorandum of the Electrical Standards Committee of the Board of Trade were also investigated with the same result.

Special experiments were made on the temperature coefficient of the E.M.F., the mean value obtained being 0.000755. When the temperature is rising, even although the rise be only a few degrees, the E.M.F. of the cell may lag considerably behind the temperature, especially if the cell be large.

The standard cells of the Board of Trade average 1.4339 volts at 25° C., or 1.4321 volts at 62° F. J. W.

Production of Hydrogen Peroxide in the Electrolysis of Aqueous Sulphuric acid. By V. KURILOFF (*J. Russ. Chem. Soc.*, **23**, 235—242).—The author has investigated the quantities of hydrogen peroxide and of persulphuric acid formed on the electrolysis of sulphuric acid solutions of different strengths. The apparatus he employed permitted the separate analysis of the liquids at the two electrodes. The hydrogen peroxide was determined by titration with potassium permanganate, and the persulphuric acid by adding a known quantity of ferrous salt to the solution and titrating back with potassium permanganate. His results are as follows:—

1. The quantity of hydrogen peroxide formed is very small.
2. Hydrogen peroxide and persulphuric acid may be formed simultaneously at both electrodes, but the peroxide is not always accompanied by persulphuric acid.
3. The formation of both products is intimately connected with the concentration. Persulphuric acid only appears when the solution contains over 10 per cent. of sulphuric acid; hydrogen peroxide when the concentration is greater than 1 per cent.
4. Mixtures containing 3, 47, and 73 per cent. of acid respectively behave differently from other mixtures with regard to the amount of hydrogen peroxide formed when they are electrolysed. This the author considers to be due to the approximation of their composition to that required by the hydrates $\text{H}_2\text{SO}_4 \cdot 150\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, and $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, which are all said by Mendeléeff to exist in solution.

J. W.

Heat of Combustion of Camphor. By BERTHELOT (*Compt. rend.*, **115**, 762—763).—Determinations of the heat of combustion of dextrogyrate camphor, by three different observers by means of the calorimetric bomb, gave as the mean results for the molecular heat of combustion +1414.2 Cal., +1413.5 Cal., and +1413.3 Cal. The general mean is +1413.7 Cal.

It follows that the heat of combustion of dextrogyrate camphor is practically identical with that of the lævogyrate and inactive forms, and is not 10 Cal. lower, as would appear from Louguinine's results.

C. H. B.

Heat of Hydration of Maleïc Anhydride. By S. TANATAR (*J. Russ. Chem. Soc.*, **23**, 252—253).—Ossipoff (*J. Russ. Chem. Soc.*, **22**, 320) calculated the heat of hydration of maleïc anhydride from the heat of solution in excess of potash, and from the heat of solution of fumaric acid in the same solvent. The author points out that this is unjustifiable, since the final states of the two systems are not the same.

J. W.

Thermochemical Data of some Organic Acids. By S. TANATAR (*J. Russ. Chem. Soc.*, **23**, 243—252).—

Levulinic Acid.

Heat of solution of solid acid, $C_5H_8O_3$	— 3·591 Cal.
Heat of neutralisation by KOH	+ 13·137 „
„ „ by NaOH	+ 13·267 „
Heat of solution in potash solution	+ 9·154 „
„ „ soda solution	+ 9·920 „
Heat of solution of $KC_5H_7O_3$	+ 1·440 „
„ „ $NaC_5H_7O_3$	+ 1·355 „
„ „ liquid $C_5H_8O_3$	— 1·393 „

Pyrotartaric Acid.

Heat of solution of $C_5H_6O_4$	— 4·894 „
Heat of neutralisation with KOH {	1st equiv. + 13·579 „
	2nd „ + 13·428 „
	total + 26·860 „
Heat of solution of acid in potash solution..	+ 22·336 „
„ „ of $K_2C_5H_6O_4$	+ 6·089 „

Racemic Acid.

Heat of solution of $C_4H_6O_6$	— 5·803 „
Heat of neutralisation by KOH {	1st equiv. + 12·955 „
	2nd „ + 12·802 „
	total + 25·735 „
Heat of solution of $K_2C_4H_4O_6 + 2H_2O$	— 10·438 „
„ „ $K_2C_4H_4O_6 + \frac{1}{2}H_2O$	— 5·834 „
„ „ $K_2C_4H_4O_6$	— 3·794 „

J. W.

Theory of Diffusion. By O. WIEDEBURG (*Zeitt physikal. Chem.*, 10, 509—516).—The author replies to the objections against his experimental methods and modes of calculation raised by Arrhenius (Abstr., 1892, 1265).

J. W.

Rise of Salt Solutions in Bibulous Paper. By E. FISCHER and E. SCHMIDMER (*Annalen*, 272, 156—169).—Schönbein's experiments have shown that when bibulous paper is dipped into an aqueous solution of a salt, the water rises more quickly than the salt, and that the relative height attained by the latter is different for different substances; it is possible therefore to recognise the presence of the several constituents of a solution by taking advantage of this difference in behaviour. The authors are of opinion that the separation referred to is brought about by the difference in the diffusibility of the dissolved substances, a view which is supported by the fact that in the case of two salts, the one with the greater diffusion velocity rises more rapidly in the bibulous paper; the diffusion phenomena of all solutions which moisten bibulous paper can, in fact, be studied in this way just as well as with the aid of membranes. The apparatus employed for the purpose consists of a glass tube, in which six cylindrical rolls of bibulous paper are placed end to end, so that they are in close contact with the walls of the tube and with one

another; the end of the tube is then dipped into the solution to be examined, and kept vertically in this position at the ordinary temperature until the 5th roll is thoroughly moistened, which is usually the case at the end of three to four days' time. The glass tube is then broken at the points where the rolls touch one another, the papers separately extracted with water, and the solutions examined.

Employing a solution of sodium chloride (10 grams) and barium chloride (10 grams) in 100 c.c. of water, the proportion of the former to the latter expressed in grams was found to be 1.022, 1.230, and 1.364 in the rolls 1, 3, and 5 respectively, showing that the more diffusible sodium salt rises more rapidly than the barium salt.

With a solution of crystalline ferrous ammonium sulphate (10 grams) in 100 c.c. of water, the proportion of iron to ammonia in the 4th roll was found to be 1 : 1.686 when the proportion in the double salt is taken as 1 : 1; with a cold saturated solution of the same salt, the proportion in the 4th roll was 1 : 1.004; and in the 5th, 1 : 0.993. Similar results were obtained with solutions of ferrous potassium sulphate and nickel potassium sulphate; the dilute solutions showed a considerable amount of dissociation, whereas in saturated solutions the dissociation was inappreciable.

Further experiments carried out in a similar manner showed that the double salts formed by mercuric chloride with the chlorides of sodium and lithium are decomposed by water, but not by alcohol; mercuric ammonium chloride, however, is not decomposed by either solvent.

The following double salts, $\text{NaH}(\text{NH}_4)\text{PO}_4 + 4\text{H}_2\text{O}$; KCN, AgCN ; $\text{KNaC}_4\text{H}_4\text{O}_6 + 4\text{H}_2\text{O}$, do not undergo dissociation in aqueous solution; the compound of dextrose with sodium chloride, $2\text{C}_6\text{H}_{12}\text{O}_6 + \text{NaCl}$, on the other hand, is partially separated into its components.

From experiments with solutions of naphthalene picrate, and of methylindole picrate in acetone and in alcohol, it would seem that no decomposition takes place.

The diffusion phenomena of ferrous ammonium sulphate, of the compound $2\text{C}_6\text{H}_{12}\text{O}_6 + \text{NaCl}$, and of mercuric sodium chloride were also examined with the aid of Rüdorff's apparatus; it was found that although the separation of the components of the first two substances in a given time is more effectively accomplished with the aid of membranes than with bibulous paper, the contrary is true in the case of the mercuric sodium chloride. F. S. K.

The Cryoscopic Behaviour of Weak Solutions. Parts V, VI, and VII. By S. U. PICKERING (*Ber.*, 25, 2012—2017, 2518—2524, and 3434—3440).—*Part V. Naphthalene and alcohol in benzene.*—These two series of results were examined in the same way as in the other cases previously described (*Abstr.*, 1892, 678, 1045). With naphthalene, the results showed two breaks; with alcohol, one; the latter results have been examined by the mathematical, as well as the graphic, method (*Phil. Mag.* [5], 33, 448), both methods leading to the same conclusion. The molecular depression in this case increases very rapidly with the dilution. *Part VI. Various substances in water*

and benzene.—In this part, the experimental details are given of determinations of which a summary has already appeared (Abstr., 1891, 971). *Part VII. General discussion of the results.* (For Parts I—IV, see Abstr., 1892, 678 and 1045).—In no case do the results obtained agree within experimental error throughout any appreciable range of strength with the values calculated according to Van't Hoff's formula corrected for supposed dissociation, nor can a single simple curve represent them without representing the error to be far larger than it is known to be. The representations of them as discontinuous curves with breaks, the positions of which were determined before the magnitude of the experimental error was known, have in every case been found to agree perfectly with this error, now that a method of determining it accurately has been obtained. The average difference (11 cases) between the apparent error of the points according to these drawings and the experimental error is only 0.4 per cent. The author quotes several instances to show that the splitting up of the figures into segments is due to the nature of the figure, and not to the method used in drawing them, and he tabulates the results, so as to show that the breaks cannot be attributed to imperfections in the thermometers used. Some evidence is also found in favour of these breaks indicating the presence of hydrates from the fact that there is a tendency for the same molecular proportions to recur in different cases; thus out of the 16 highest hydrates indicated there is one group of four in which the water molecules present are practically identical, two groups of three each, and two groups of two each; it is possible also that there may be a simple numerical relationship between the water molecules in higher and lower hydrates.

S. U. P.

Melting Points of Solvents as the Inferior Limit of Solubilities. By A. ETARD (*Compt. rend.*, 115, 950—953).—The solubility of naphthalene in hexane varies from 0.3 per cent. at -50° , the lower limit, to 78.8 at 70° ; of triphenylmethane, from 1.2 per cent. at -30° to 97.1 per cent. at 90° ; of diphenylamine, from 0.5 per cent. at -30° to 94.5 per cent. at 50° . That of naphthalene in carbon bisulphide varies from 1.2 per cent. at -60° to 90.3 at 70° ; of triphenylmethane, from 3.4 at -60° to 92.2 at 80° ; of diphenylamine, from 1.3 at -60° to 76.0 at 30° ; of phthalic anhydride, from 0.03 at -40° to 30.2 at 180° . That of naphthalene in chloroform varies from 6.6 at -40° to 87.2 at 70° ; of triphenylmethane, from 10.5 at -50° to 88.7 at 80° . The lines of solubility, which are in every case curved, are to be regarded as the loci of the melting points of mixtures of the solvent and dissolved substance.

JN. W.

Cailletet and Colardeau's Method of determining Critical Points. By G. P. GRIMALDI (*Real. Accad. Linc.*, 1892, i, 79—86).—The author criticises Cailletet and Colardeau's method of determining the critical temperature of liquids (Abstr., 1891, 779). By applying the method to the isothermals obtained by Amagat for carbonic anhydride, it is shown that the critical temperature lies between 28° and 35° . Further, an examination of the results obtained by Cailletet and Colardeau leads to the conclusion that the critical temperature of

water is only determined by their method within $\pm 5^\circ$. The accuracy which Hinrichs (Abstr., 1892, 396) attributes to their determinations is hence impossible.

W. J. P.

Effects of Gravity on Fluids at the Critical Point. By GOUY (*Compt. rend.*, 115, 720—722).—In all work with reference to the critical point, no attention has been paid up to the present to the compression of the fluid by its own weight, doubtless because the differences in the pressure produced in this manner appear inconsiderable when compared with the pressure of the fluid itself. But since at the critical point the compressibility is infinite, and very large in its neighbourhood, this is by no means the case. The author, selecting the case of carbonic anhydride, shows that the weight of the fluid exercises a very considerable influence on the results at the critical point.

H. C.

Velocity of Sugar Inversion in presence of Acetic and Lactic acids. By A. SPERANSKY (*J. Russ. Chem. Soc.*, 23, 147—150).—The following table contains the velocity constants of sugar inversion at 50° for solutions of lactic and acetic acids with or without the addition of salts. Equal volumes of the acid solution and of a 20 per cent. sugar solution were taken.

Solution.		Velocity constant.
Normal acetic acid	2.55
$\frac{1}{2}$ -normal	1.52
„	+ $\frac{1}{2}$ -normal NaCl	2.67
Normal lactic acid	10.29
$\frac{1}{2}$ -normal	6.88
„	+ $\frac{1}{2}$ -normal NaCl	10.02
„	+ Na ₂ SO ₄	4.40
„	+ $\frac{1}{2}$ -normal sodium lactate ..	very small.

An equivalent quantity of barium chloride had nearly the same effect as sodium chloride.

The addition of sodium or barium chloride thus increases the velocity of reaction, whilst the addition of sodium sulphate diminishes it.

J. W.

General Method of Chemical Synthesis. By R. PICTET (*Compt. rend.*, 115, 708—712, and 814—817).—According to the theory which the author holds, all chemical action should be impossible at very low temperatures, and a series of very interesting experiments has been executed in order to show that this is the case. Aqueous sulphuric acid, containing 89 per cent. H₂SO₄ and solidifying at -56° , was brought when in the solid condition and at -125° into intimate contact with finely powdered sodium hydroxide, also at -125° , and the two strongly compressed without any sign of chemical change occurring. The passage of electric sparks through the mass only causes action to take place in the path of the sparks, but this action is not communicated to the rest of the mixture. On warming, action suddenly commences at -80° , the heat evolved and

abrupt change of temperature causing breakage of the vessel containing the mixture. With sulphuric acid containing 35 per cent. H_2SO_4 and solidifying at -88° , similar results were obtained. Potassium hydroxide employed in place of sodium hydroxide remains in like manner unacted on below -90° . Concentrated ammonia and sulphuric acid do not act at all on one another below -80° ; above this temperature, a limited action takes place under the action of electric sparks, and at -60 – 65° complete action suddenly occurs. Sulphuric acid and common salt do not react below -50° ; from -50° to -25° there is limited action, and then complete action occurs. With the carbonates of calcium and sodium and 35 per cent. H_2SO_4 , there is no action at -80° . The first bubbles of gas make their appearance at -56° with sodium carbonate, and at -52° with calcium carbonate, and the reaction becomes turbulent at -15° with calcium, and at -30° with sodium carbonate. All other carbonates behave similarly. With nitric acid in place of sulphuric acid, similar results were obtained in all the above cases, chemical action commencing, however, at a slightly lower temperature in each case. Metallic sodium, when brought into contact with aqueous alcohol, containing 84 per cent. alcohol, at -78° , undergoes no change. Action only commences at -48° , and then proceeds briskly. Sodium and 35 per cent. H_2SO_4 may be mixed at -85° without any action occurring, but, when heated up to -50° , a violent action suddenly commences, the hydrogen evolved inflaming spontaneously. Metallic potassium acts in a similar manner, but in this case change sets in at -68° instead of -50° . If sulphuric acid and an alcoholic solution of barium chloride are mixed at -85° , no change occurs, a precipitate first appearing when the solution is heated to -70° . At -40° the reaction is complete. Alcoholic silver nitrate and hydrochloric acid were mixed at -125° without reaction. At -90° action commenced, and was complete at -80° . Potassium hydroxide in alcoholic solution and phenolphthalein were mixed at -135° without any change occurring; a faint red tinge appeared at -100° , and the colour was pronounced at -80° . Litmus in contact with sulphuric and hydrochloric acids remains blue at -120° , a sudden change to red taking place in the one case at -105° , and in the other at -110° .

As general result of these observations, the author concludes that no action whatever takes place between the temperatures -125° and -155° , no matter what the nature of the reacting substances.

H. C.

Inorganic Chemistry.

Combustion of Hydrogen in Nitrous Oxide. By C. MONTMARTINI (*Real. Accad. Linc.*, 7, ii, 219–222).—The author finds that on passing mixtures of nitrous oxide with small quantities of hydrogen over palladium-black, the hydrogen is completely converted into water in accordance with the equation $\text{H}_2 + \text{N}_2\text{O} = \text{N}_2 + \text{H}_2\text{O}$.

The apparatus employed consists of a gas burette, containing the mixture of nitrous oxide and hydrogen, connected with a gas pipette by means of a glass tube containing palladium-black; both the tube and the burette are surrounded by water jackets, as an appreciable amount of heat is evolved in the condensation. The gas is passed four or five times over the palladium to ensure complete conversion of the hydrogen. The estimation of hydrogen by this method cannot be performed in presence of nitric oxide, owing to the absorption of the latter by palladium. It was found that 1 vol. of the metal at 18° absorbed 420·1 vols. of nitric oxide in two days with evolution of heat.

W. J. P.

Hydrogen Bromide. By E. LÉGER (*Compt. rend.*, 115, 946—948).—A convenient method of preparing hydrogen bromide in quantity is to drop strong sulphuric acid from a tap-funnel on solid potassium bromide heated in a stoppered, tubulated retort on the water-bath. The gas given off is contaminated with small quantities of sulphurous anhydride and bromine, from which it is freed by two sets of wash-bottles, the first of which contains a strong solution of bromine in hydrobromic acid, the second, amorphous phosphorus suspended in hydrobromic acid. When all the sulphuric acid has been added, and the evolution of gas has slackened, the retort may be heated over a flame.

Another method is to pass sulphurous anhydride through a solution of bromine (1 vol.) in concentrated hydrobromic acid (1 vol.). The evolved hydrogen bromide is then purified as above.

JN. W.

Constitution of Hydroxylamine. By S. S. KOLOTOFF (*J. Russ. Chem. Soc.*, 23, 3—5).—In view of the fact that hydroxyl compounds of nitrogen give up more or less readily the elements of water to form new nitrogen compounds, the author attempted to bring about the following reaction:— $\text{NH}_2\cdot\text{OH} + \text{NH}_3 = \text{N}_2\text{H}_4 + \text{H}_2\text{O}$. Experiment showed, however, that this reaction does not take place, even on heating at 100° for 24 hours. He is therefore of opinion that free hydroxylamine contains no hydroxyl, but is represented by the formula $\text{H}_3\text{N}\cdot\text{O}$.

When a salt of hydroxylamine is treated in Hentschel's nitrogen apparatus with bromine dissolved in excess of strong soda, only half of the nitrogen it contains is evolved in the free state, the other half being probably oxidised to acid. The reaction may be regarded as taking place according to the equation $2\text{NH}_3\text{O} = \text{NH}_3 + \text{HNO} + \text{H}_2\text{O}$, the ammonia being then oxidised. In order to test this view, the author oxidised in the cold a weighed quantity of a salt of hydroxylamine in a large excess of soda with the quantity of bromine calculated from the above equation. After the oxidation was completed, the excess of soda was neutralised with hydrochloric acid, and excess of copper sulphate added to the solution. The yellowish precipitate, which at once appeared, settled readily, and, after being collected and washed with water, was dried over sulphuric acid at the ordinary temperature, and weighed. The calculated quantity of $\text{Cu}(\text{NO})_2$ obtainable, according to the equation from the amount of hydroxylamine salt taken, was 4·3 grams; the weight of the precipi-

tate was 4.9 grams, corresponding with the formula $\text{Cu}(\text{NO})_2 \cdot \text{H}_2\text{O}$, which was confirmed by a determination of the copper in the precipitate. The copper salt does not lose weight at 136° , and blackens when treated with soda. The author considers it to be the dihydrogen cupric salt of "pyrohyponitrous acid," $\text{H}_4\text{N}_2\text{O}_3$.

Hydroxylamine sulphate loses weight at $125\text{--}130^\circ$, rapidly at 136° , 28.4 per cent. being the maximum loss. The ratio between the nitrogen and sulphur in the residue would appear to point to the formation of salts of N_2H_4 and N_2H_5 . J. W.

Action of Sulphurous Anhydride on Oxy-salts. By W. R. HODGKINSON and J. YOUNG (*Chem. News*, 66, 199).—The exposure of nitrates to a current of dry sulphurous anhydride results in their complete conversion into sulphates, with the evolution of nitrous fumes; the reaction is accompanied by a rapid rise in temperature, which occasions an explosion if the treatment is applied to gunpowder. Chlorates, by similar treatment, are also converted into sulphates, with the evolution of chlorine peroxide, which, at temperatures above 60° , decomposes with a flash and the production of sulphuric anhydride. Moist sulphurous anhydride acts more vigorously on chlorates than the dry gas; but, in most cases, without the visible liberation of chlorine peroxide. Dropping some alcoholic or ethereal solution of sulphurous anhydride on to powdered potassium chlorate causes the evolution of white fumes and a sharp explosion. The action of dry sulphurous anhydride on silver chromate results, apparently, in the formation of silver sulphate and chromic oxide; but with alkali chromates, dichromates, or permanganates, a partial conversion of the chromium or manganese into sulphate accompanies the formation of the alkali sulphate; the latter reaction goes on with rapidity at first.

D. A. L.

Graphochemistry of Gunpowder. By E. NICKEL (*Zeit. physikal. Chem.*, 10, 454—458).—The author supposes gunpowder to consist of a mixture $m\text{KNO}_3 + n\text{C} + p\text{S}$, and on this basis finds graphically the limits between which the composition of a good powder must lie (compare Abstr., 1892, 1158). J. W.

Molecular Weights of Sodammonium and Potassammonium. By A. JOANNIS (*Compt. rend.*, 115, 820—823).—Determinations of the vapour pressures of solutions of naphthalene in liquefied ammonia show that this liquid behaves as a normal solvent.

Measurements of the vapour pressures and of the boiling points of solutions of sodammonium and potassammonium in liquid ammonia show that the molecules of these compounds are represented by the formulæ $\text{Na}_2\text{N}_2\text{H}_6$ or $\text{NaH}_3\text{N} \cdot \text{NH}_3\text{Na}$ and $\text{K}_2\text{N}_2\text{H}_6$ or $\text{KH}_3\text{N} \cdot \text{NH}_3\text{K}$ respectively. C. H. B.

Silver Hemisulphate. By M. C. LEA (*Amer. J. Sci.* [3], 44, 322—329).—Silver hemisulphate is obtained by the action of hypophosphorous acid and sulphuric acid on silver nitrate, phosphate, or carbonate; the last gives the best results, the action with the nitrate being too rapid, and that with the phosphate too slow. The most

convenient method is as follows:—40 grams of silver nitrate is precipitated with sodium carbonate, and the precipitate is well washed and mixed with a solution of 100 grams of sodium hypophosphite in 650 c.c. of water, to which 4 c.c. of sulphuric acid has been added. After a few minutes, a further quantity of sulphuric acid, 6 c.c., previously diluted with a little water, is added, and the mixture agitated until a bluish-black film of reduced silver begins to form on the surface, and at this point further reduction is prevented by neutralising the liquid with sodium carbonate. The reaction is usually complete in 20 to 25 minutes.

It is important that all the reagents should be free from halogens, and the solution of sodium hypophosphite before being acidified should be mixed with a small quantity of silver nitrate solution, allowed to remain, with occasional agitation, for several hours, and then filtered in order to remove the silver chloride.

The silver nitrate may be precipitated with sodium phosphate, but in this case about 24 hours is required for reduction.

The crude product is washed several times by decantation, and is then treated with nitric acid of sp. gr. 1.42 diluted with three times its volume of water, the quantity used being about twice the volume of the moist precipitate left after decanting the water. The acid is left in contact with the precipitate for three or four hours, and is then poured off, and the precipitate is well washed. After three successive treatments with acid in this way, the precipitate is very thoroughly washed with boiling water, and is then dried by exposure to air or at 100°.

The same product is obtained under a variety of conditions, and seems to be formed whenever a silver salt is brought into contact with a hypophosphite acidified with sulphuric acid. Hypophosphorous acid, however, has very little action on ready formed silver sulphate.

The colour of the silver hemisulphate thus obtained is bright brown, and is permanent when exposed to air, but changes to violet on heating for some time at 160°. No sulphuric acid is given off, even at a dull red heat. (In another part of the paper, the author states that the terra cotta or warm brown shade of the moist substance changes to pale lilac, by drying above 100°, becomes greyish at 165—170°, and yellowish-green at a higher temperature. Considerably below a red heat it acquires a fine ruby colour, which darkens almost to black during cooling, but then becomes paler, the cooled substance being pale olive-green.) Strong sulphuric acid is without action even at 100°; dilute nitric acid has very little effect, but the acid of sp. gr. 1.42 gradually dissolves the salt; ferrous sulphate is without action even after several days.

Alkali hydroxides slowly but completely convert the hemisulphate into a mixture of the hemioxide and the ordinary oxide, and the quantity of oxygen given off when this precipitate is strongly heated agrees with the constitution ascribed to the salt.

Hydrochloric and hydrobromic acids, and alkali chlorides and bromides, yield mixtures of the hemihalides and the ordinary halides, which spontaneously decompose into mixtures of the ordinary halides and metallic silver, the black colour of the hemihalide giving place

to the grey colour of metallic silver. The composition of the freshly obtained product agrees with the constitution ascribed to the hemisulphate.

The hemisulphate prepared in the manner described has the composition Ag, 76.44; O, 3.29; P_2O_5 , 2.19; SO_3 , 16.33; H_2O , 1.78 = 100.03, which agrees fairly well with the formula $7(Ag_4SO_4, Ag_2SO_4, H_2O) + Ag_6PO_4, Ag_3PO_4$. The quantity of phosphoric anhydride present is always about 2 per cent., and it cannot be removed even by treatment with hot strong sulphuric acid.

If the phosphoric acid is regarded simply as an impurity, the composition of the salt is $Ag_4SO_4, Ag_2SO_4 + H_2O$.

The author is of opinion that during the preparation of the salt the hemisulphate is produced in considerable excess, but is decomposed on treatment with nitric acid, the product being stable only when the ordinary salt and the hemi-salt are combined in molecular proportion.

Other hemi-salts of silver and oxy-acids probably exist, but they cannot be obtained by acting on the ordinary salts with hypophosphorous acid, although possibly they may be produced when the normal salts are formed in presence of sodium hypophosphite. The precipitate formed by adding silver nitrate to a solution of sodium citrate and sodium hypophosphite free from chlorides yields a rose-red solution when placed in a large quantity of water containing a small quantity of ammonia.

C. H. B.

Fusion of Calcium Carbonate. By H. LE CHATELIER (*Compt. rend.*, 115, 817—820).—Chemically pure calcium carbonate in the form of an impalpable powder was enclosed in a steel cylinder and compressed between two steel pistons with a pressure of 1000 kilos. per square centimetre. A spiral of platinum wire embedded in the powder was heated by an electric current. Under these conditions, the calcium carbonate in the neighbourhood of the spiral can be fused without difficulty, there being a sharp line of demarcation between the part which has melted, and consequently become translucent, and that which has simply agglomerated under the pressure. A thin section of the fused portion shows minute crystals, and resembles certain specimens of marble that are but slightly macted.

The melting point of calcium carbonate under pressure approaches closely to the melting point of gold, but is not quite so high, a result which confirms the earlier observations of J. Hall.

C. H. B.

Fusion of Calcium Carbonate. By A. JOANNIS (*Compt. rend.*, 115, 934—936).—The fusion of calcium carbonate effected by Le Chatelier (preceding abstract) and Hall (*Journ. de Phys. de la Métherie*, 61, 197, and 64, 461), at a temperature between the melting points of silver and gold, and under a mechanical pressure of 300—1000 kilos. per sq. cm., was probably, to a large extent, the direct effect of the latter, in accordance with the well-known physical law. The author finds that neither the pure carbonate nor chalk melts when heated in a closed platinum vessel to a temperature even above the melting point of gold, although the pressure of the dis-

sociated carbonic anhydride may rise to 17 atmos. At the higher temperatures, the product, however, is crystalline, and resembles marble.

JN. W.

Zincoides of the Alkaline Earths. By G. BERTRAND (*Compt. rend.*, 115, 939—941).—*Calcium zincoxide*, $\text{Zn}_2\text{CaH}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, is obtained in brilliant, lozenge-shaped plates when ammonia is withdrawn from the ammoniacal solution of its proximate constituents. It absorbs carbonic anhydride rapidly from the air, becoming opaque, and is decomposed by water into zinc oxide and lime. It does not lose water at 125° , but is decomposed at a dull-red heat. *Strontium zincoxide*, $\text{Zn}_2\text{SrH}_2\text{O}_3 + 7\text{H}_2\text{O}$, made in a similar way, crystallises in flattened, lozenge-shaped plates. *Barium zincoxide*, $\text{Zn}_2\text{BaH}_2\text{O}_3 + 7\text{H}_2\text{O}$, crystallises in brilliant, flattened needles. These zincoides may have the constitution $\text{M}''(\text{O} \cdot \text{ZnOH})_2 + x\text{Aq}$.

JN. W.

Action of Ammonia on Sulphates. By W. R. HODGKINSON and C. C. TRENCH (*Chem. News*, 66, 223).—On heating silver, mercury, and bismuth sulphates to the melting point of zinc in a current of dry ammonia, they are entirely reduced; and, at a red heat, lead and thallium sulphates are completely decomposed, yielding a small quantity of the respective sulphides. Ferrous sulphate, anhydrous, crystalline, or as the double ammonium salt, is reduced, by the action of gaseous ammonia, to oxide containing 1 to 2 per cent. of sulphur; whilst the sulphates of zinc, magnesium, cobalt, nickel, manganese, and chromium, under similar circumstances, yield mixtures of oxide and sulphide in nearly molecular proportions. Copper sulphate, anhydrous or crystalline, absorbs ammonia, melts below 200° , turns black, appears to boil, and at about 400° decomposes with incandescence, leaving almost pure copper. The main volatile product is ammonium thionamate, and this, in a cooled receiver, where it comes in contact with the water, which is another product of the reaction, gives rise to ammonium sulphite; there is no ammonium sulphate, but probably a hydrazine compound is formed.

D. A. L.

Double Salt of Lead and Potassium Iodides. By F. A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 10, 467—476; compare *Abstr.*, 1892, 560).—The double salt of lead and potassium iodides is not $\text{PbI}_2 \cdot 2\text{KI} \cdot 2\frac{1}{2}\text{H}_2\text{O}$, as the author assumed from Ditte's analysis, but $\text{PbI}_2 \cdot \text{KI} \cdot 2\text{H}_2\text{O}$. The conclusions previously arrived at have, from this cause and from a more extended investigation, to be altered as follows:—

The double salt $\text{PbI}_2 \cdot \text{KI} \cdot 2\text{H}_2\text{O}$ has neither a proper melting point nor a proper solubility. It can only exist in contact with solutions in which the ratio of potassium to lead is greater than the ratio K : Pb. At elevated temperatures, the double salt in contact with the solution is decomposed into another double salt containing only half a molecule of water, the ratio of the two iodides being unknown. There is probably no temperature of transformation for either of these double salts into their components.

J. W.

A New Double Salt. By W. MEYERHOFFER (*Monatsh.*, 13, 716—741).—The author describes the methods by which he has determined the conditions under which the double salt, $\text{CuCl}_2 \cdot \text{LiCl} \cdot 2\text{H}_2\text{O}$, exists in contact with water. The results obtained are of no general interest.

G. T. M.

Graphochemistry of Lime Soda Glasses. By E. NICKEL (*Zeit. physikal. Chem.*, 10, 450—453).—In this paper, the author applies the principles described in *Abstr.*, 1892, 1158, to the discussion of the composition of lime soda glasses.

J. W.

Hydrates of Ferric Chloride. By H. W. B. ROOZEBOOM (*Zeit. physikal. Chem.*, 10, 477—503).—The author has made a comprehensive investigation of the hydrates of ferric chloride, studying in especial the solubility curves of these hydrates in water. They are four in number, namely, $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$; $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$; $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$, and $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$. Only the first and third of these were previously known, the composition of the latter being uncertain. The hydrate $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$ forms aggregates of small, well-characterised, monoclinic crystals, very strongly dichroic, the colours varying between yellow and blue. They are much lighter in colour than those of the pentahydrate, and not nearly so deliquescent. The hydrate $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ forms rhombic crystals, showing a dichroism from yellow to brown.

The melting points of the four hydrates lie at 37° , 32.5° , 56° , and 73.5° respectively. Below these points, each can exist in equilibrium with solutions containing either more or less water than itself. These saturated solutions form two branches of the solubility curve, which join without a break at the melting point. The curve for the solutions of a hydrate containing more water than itself cuts at a definite point the curve for the solutions of the next higher hydrate containing less water than itself. At such points, the solutions solidify to mixtures of both hydrates. In the case of the extreme hydrates, ice appears on the one hand, and anhydrous ferric chloride on the other. These "cryohydric" points are at -55° , 27.4° , 30° , 55° , and 66° , respectively. Many phenomena of supersaturation were observed, all of which could be deduced from the nature of the solubility curves. The following determinations of the vapour pressure at 15° were made:—

	Vapour pressure in mm. mercury.
$\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ with weaker solution	6.0
$\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$	2.3
$\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ with $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$	1.8
$\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ with stronger solution	1.4
$\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$ with weaker solution	1.3

The heats of solution of the hydrates with 12, 7, and 5 mols. H_2O at 15° pass from positive to negative values with increasing concentration of the solution; in saturated solutions, they are negative, which corresponds with the increase of solubility with rise of temperature.

The following tables exhibit the composition of the various solutions in equilibrium with the solids mentioned:—

$n' = \text{mols. Fe}_2\text{Cl}_6 \text{ to } 100 \text{ mols. H}_2\text{O.}$
 $n'' = \text{,, H}_2\text{O} \text{ ,, } 1 \text{ mol. Fe}_2\text{Cl}_6.$

Ice.

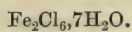
$t.$	$n'.$	$n''.$
0	0	∞
-10	1.00	100
-20.5	1.64	61
-27.5	1.90	52.6
-40	2.37	42.2
-55	2.75	36.4

 $\text{Fe}_2\text{Cl}_6, 5\text{H}_2\text{O.}$

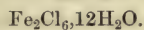
$t.$	$n'.$	$n''.$
12	12.87	7.77
20	13.95	7.17
27	14.85	6.73
30	15.12	6.61
35	15.64	6.40
50	17.50	5.71
55	19.15	5.22
56	20.00	5.00
55	20.32	4.92

 $\text{Fe}_2\text{Cl}_6, 4\text{H}_2\text{O.}$

$t.$	$n'.$	$n''.$
50	19.96	5.01
55	20.32	4.92
60	20.70	4.88
69	21.53	4.64
72.5	23.35	4.28
73.5	25.00	4.00
72.5	26.15	3.82
70	27.90	3.58
66	29.20	3.43



<i>t.</i>	<i>n'</i> .	<i>n''</i> .
20°	11·35	8·81
27·4	12·15	8·23
32	13·55	7·38
32·5	14·29	7·00
30	15·12	6·61
25	15·54	6·47



<i>t.</i>	<i>n'</i> .	<i>n''</i> .
-55°	2·75	36·4
-41	2·81	35·6
-27	2·98	33·6
0	4·13	24·2
10	4·54	22·0
20	5·10	19·6
30	5·93	16·9
35	6·78	14·8
36·5	7·93	12·6
37	8·33	12·0
36	9·29	10·8
33	10·45	9·57
30	11·20	8·92
27·4	12·15	8·23
20	12·83	7·80
10	13·20	7·57
8	13·70	7·30



<i>t.</i>	<i>n'</i> .	<i>n''</i> .
66°	29·20	3·43
70	29·42	3·40
75	28·92	3·46
80	29·20	3·43
100	29·75	3·33

Anhydrous and Crystalline Iron Fluorides. By G. POULENC (*Compt. rend.*, **115**, 941—944).—Ferrous fluoride, FeF_2 , made by passing air-free hydrogen fluoride over red-hot iron or anhydrous ferric chloride, crystallises in small, branching, colourless, rhombic prisms, which turn yellow on exposure to the air. The sp. gr. is 4.09. When heated with sulphuric acid, sodium carbonate, air, hydrogen, steam, or hydrogen chloride, it is decomposed, the reaction in the last-named case being the reverse of that involved in its formation. Ferric fluoride, Fe_2F_6 , is prepared by passing hydrogen fluoride over red-hot iron, ferric oxide, hydrated ferric fluoride, or ferric chloride, or by projecting the hydrated fluoride into fused ammonium chloride, and heating the product in a current of inert gas. It does not fuse, even at 1000° , although it partially volatilises and partially crystallises at that temperature, forming small, highly refractive, greenish crystals of sp. gr. 3.87. It is only slightly attacked by nitric, hydrochloric, and sulphuric acids, but is decomposed into ferric oxide by heating in contact with air, and is reduced by hydrogen at a dull-red heat. When heated in steam, it is decomposed into ferric oxide and hydrogen fluoride, whilst with hydrogen chloride or sulphate, ferric chloride or sulphate and hydrogen fluoride are formed. It is decomposed also by fusion with sodium carbonate. JN. W.

Preparation of Metallic Chromium by Electrolysis. By E. PLACET (*Compt. rend.*, **115**, 945).—The solution to be electrolysed contains chrome alum and an alkali sulphate, and is acidified with sulphuric acid. The metallic chromium is deposited at the cathode as a hard, bluish-white, lustrous metal, which, under certain conditions, crystallises in groups resembling the branching of firs. It does not oxidise in the air, and is not attacked by strong nitric or sulphuric acid or potash. Other metals may be plated with chromium, and the surface so obtained resembles "oxidised" silver. Chromium forms many alloys. JN. W.

Cryoscopic Behaviour of Aqueous Solutions of the Violet and Green Chromic Chlorides. By G. MARCHETTI (*Real. Accad. Linc.*, 1892, i, 215—217, and *Gazzetta*, **22**, ii, 375—379).—The author has prepared the violet and green modifications of chromic chloride by Recoura's method (*Abstr.*, 1886, 508), and finds them to have the composition $\text{Cr}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ when dried over sulphuric acid, not $\text{Cr}_2\text{Cl}_6 \cdot 13\text{H}_2\text{O}$, as found by Recoura.

The molecular depression of the freezing point of water by the two chlorides is very different; that caused by the violet modification being much the greater. The hydrolytic dissociation is far advanced in both cases; the molecular depression for the violet modification is approximately equal to that obtained with ferric chloride.

W. J. P.

Complex Acids containing Heptavalent Iodine. By C. W. BLOMSTRAND (*Zeit. anorg. Chem.*, **1**, 10—50; compare *Abstr.*, 1887, 327; 1890, 107).—The author first discusses the probability of the iodine atom in periodic acid being septavalent, and compares it with the quinquivalent phosphorus atom in phosphoric acid, which acid

contains the tervalent group PO, just as periodic acid contains the quinquivalent group IO. He then shows that this view of the constitution of periodic acid affords an explanation of the constitution of the salts of certain complex acids which he has prepared, which contain periodic acid united with varying quantities of molybdic acid. These salts may be divided into three groups derived respectively from *hexamolybdoperiodic acid*, $\text{IO}(\text{OH})_2(\text{O} \cdot \text{MoO}_2 \cdot \text{O} \cdot \text{MoO}_2 \cdot \text{OH})_3$, *monomolybdoperiodic acid*, $\text{IO}(\text{OH})_4 \cdot \text{O} \cdot \text{MoO}_2 \cdot \text{OH}$, and *tetramolybdoperiodic acid*, $\text{IO}(\text{OH})_3(\text{O} \cdot \text{MoO}_2 \cdot \text{O} \cdot \text{MoO}_2 \cdot \text{OH})_2$.

Hexamolybdoperiodates.—These were prepared by heating the periodate of the metal, or periodic acid itself, with molybdic acid and the carbonate of the metal in water until solution had taken place, and allowing the resulting solution to crystallise, best at the ordinary temperature. They were also obtained by making a dilute solution of the free acid from barium molybdate, periodic acid, and sulphuric acid, and neutralising this solution with the carbonate of the metal. This dilute aqueous solution of the free acid, when evaporated, yielded a transparent, amorphous mass, without a trace of crystalline structure. The *sodium salt*, $\text{Na}_5\text{Mo}_6\text{IO}_{24}$, crystallises with $17\text{H}_2\text{O}$ in rhombohedra, $a : c = 1 : 1.9635$, and with $13\text{H}_2\text{O}$ in triclinic plates, $a : b : c = 1.0557 : 1 : 1.1072$; $\alpha = 127^\circ 57'$, $\beta = 60^\circ 51'$, $\gamma = 79^\circ 37'$. The *potassium*, or more strictly *potassium hydrogen salt*, $\text{K}_5\text{Mo}_6\text{IO}_{24} + \text{KHM}_6\text{IO}_{24} + 12\text{H}_2\text{O}$, forms four- or six-sided triclinic plates, somewhat analogous to, but not isomorphous with, those of the sodium salt, $a : b : c = 0.7497 : 1 : 0.9708$; $\alpha = 101^\circ 9\frac{1}{2}'$, $\beta = 68^\circ 10'$, $\gamma = 80^\circ 34'$. The *lithium salt*, $\text{Li}_5\text{Mo}_6\text{IO}_{24}$, crystallises with $15\text{H}_2\text{O}$ in a rhombohedral form, $a : c = 1 : 1.8823$, and with $9\text{H}_2\text{O}$ in a second form with prismatic habit, which could not be determined crystallographically. The *ammonium salt*, $(\text{NH}_4)_5\text{Mo}_6\text{IO}_{24} + 6\text{H}_2\text{O}$, crystallises in two triclinic varieties, of which the first and most commonly occurring is isomorphous with the potassium salt, while the second forms hexagonal plates; (1.) $a : b : c = 0.7417 : 1 : 0.9550$; $\alpha = 122^\circ 43'$, $\beta = 69^\circ 2'$, $\gamma = 75^\circ 29\frac{1}{2}'$; (2.) $a : b : c = 0.4973 : 1 : 0.5770$; $\alpha = 83^\circ 35'$, $\beta = 86^\circ 17'$, $\gamma = 78^\circ 4'$. *Calcium salts*.— $\text{Ca}_5(\text{Mo}_6\text{IO}_{24})_2 + 26\text{H}_2\text{O}$, forms ill-defined crystals; $\text{Ca}_2\text{HMo}_6\text{IO}_{24} + 10\text{H}_2\text{O}$, slender prisms. The *strontium sodium salt*, $\text{Sr}_2\text{NaMo}_6\text{IO}_{24} + 10\text{H}_2\text{O}$, forms crusts of microscopic prisms. The *barium sodium salt*, $\text{Ba}_5(\text{Mo}_6\text{IO}_{24})_2 + 2\text{Ba}_2\text{NaMo}_6\text{IO}_{24} + 28\text{H}_2\text{O}$, also forms long prisms. The *manganese sodium salt*, $\text{MnNa}_3\text{Mo}_6\text{IO}_{24} + 16\text{H}_2\text{O}$, forms apparently rhombohedral crystals. These last three salts were prepared by the addition of strontium, barium, and manganese chlorides respectively to a solution of the sodium salt.

Ammonium sodium monomolybdoperiodate, $(\text{NH}_4)_2\text{NaH}_2\text{MoIO}_9 + 4\text{H}_2\text{O}$, is obtained by treating the sodium hexa-salt with ammonia; it crystallises in quadrangular, triclinic plates similar to, if not isomorphous with, the potassium and sodium hexa-salts, $a : b : c = 0.6953 : 1 : 0.8662$; $\alpha = 97^\circ 7'$, $\beta = 75^\circ 30'$, $\gamma = 80^\circ 36'$.

Ammonium tetramolybdoperiodate, $(\text{NH}_4)_4\text{HMo}_4\text{IO}_{18} + 3\text{H}_2\text{O}$, is obtained by treating the ammonium salt of the hexa-acid with ammonia; it forms prismatic crystals.

C. F. B.

Action of Hydrogen Peroxide on certain Fluorides and Oxyfluorides. By A. PICCINI (*Zeit. anorg. Chem.*, 1, 51—64).—Compounds are formed which contain oxygen in the same state as in hydrogen peroxide; it is given off when the compound is heated or treated with permanganate. *Potassium fluoroxypermolybdate*, $\text{MoO}_3\text{F}_2 \cdot 2\text{KF} + \text{H}_2\text{O}$, was prepared by dissolving the fluoroxymolybdate, $\text{MoO}_2\text{F}_2 \cdot 2\text{KF} + \text{H}_2\text{O}$ (obtained by treating molybdic acid with hydrofluoric acid and potassium fluoride), in 4 per cent. hydrogen peroxide, and recrystallising the product from aqueous hydrogen peroxide containing a little hydrofluoric acid. It forms yellow, transparent, monoclinic tables, $a : b : c = 1.2394 : 1 : 1.9928$; $\beta = 50^\circ 28'$, is stable in air, loses water, at 100° , oxygen at 150° , and, when heated in air, yields potassium molybdate, KMoO_4 , when in a vacuum, the fluoroxymolybdate, $\text{Mo}_2\text{F}_2 \cdot 2\text{KF}$. *Rubidium fluoroxypermolybdate*, $\text{MoO}_3\text{F}_2 \cdot 2\text{RbF} + \text{H}_2\text{O}$, was prepared by adding a hydrofluoric acid solution of molybdic acid to a hydrogen peroxide solution of rubidium chloride. It forms long, narrow plates or prisms which are monoclinic, $a : b : c = 1.27415 : 1 : 2.0619$, and isomorphous with the potassium salt, which it resembles in its properties. *Cæsium fluoroxypermolybdate*, $\text{MoO}_3\text{F}_2 \cdot 2\text{CsF} + \text{H}_2\text{O}$ (?), prepared like the rubidium salt, forms yellow plates which probably have the composition given. *Triammonium fluoroxypermolybdate*, $\text{MoO}_3\text{F}_2 \cdot 3\text{NH}_4\text{F}$, is formed by adding hydrogen peroxide and an excess of ammonium fluoride to a hydrofluoric acid solution of ammonium molybdate; also by the action of hydrogen peroxide on both of the fluoroxymolybdates $\text{MoO}_2\text{F}_2 \cdot 3\text{NH}_4\text{F}$ and $\text{MoO}_2\text{F}_2 \cdot 2\text{NH}_4\text{F}$. It forms sometimes pointed, sometimes flattened, yellow prisms, which, when heated above 100° , lose weight, and leave a residue of molybdic anhydride. C. F. B.

Fluoroxymolybdates: the Non-existence of Cuprous Fluoride. By F. MAURO (*Real. Accad. Linc.*, 1892, i, 194—203).—*Cupric fluoroxypermolybdate*, $\text{MoO}_3\text{F}_2 \cdot \text{CuF}_2 \cdot 4\text{H}_2\text{O}$, separates in transparent, blue, six-sided plates from a hydrofluoric acid solution of molybdic anhydride and copper oxide in molecular proportion; the crystals are monosymmetric, $a : b : c = 1.4828 : 1 : 1.0987$, $\beta = 85^\circ 9'$. The substance is unaltered by dry air, but readily absorbs moisture from the atmosphere, yielding a pasty mass, which subsequently dries, leaving a blue powder. The crystals lose weight and become light green at 115° , and begin to evolve hydrogen fluoride at 135° . *Cupric fluoroxyhypomolybdate*, $\text{MoOF}_3 \cdot \text{CuF}_2 \cdot 4\text{H}_2\text{O}$, is prepared by heating cuprous oxide with a solution of molybdic anhydride in hydrofluoric acid in an atmosphere of carbonic anhydride, the solution being first reduced electrically as in the preparation of the fluoroxyhypomolybdates of potassium and ammonium (*Abstr.*, 1890, 702); the solution deposits a mixture of red octahedra of metallic lustre, now under examination, and cupric fluoroxyhypomolybdate. The latter forms blue, monosymmetric crystals, $a : b : c = 1.4745 : 1 : 1.0929$, $\beta = 85^\circ 43'$, which deliquesce in the air with separation of metallic copper; it crystallises unchanged from hydrofluoric acid, but is decomposed by water, copper being deposited. The salt possesses reducing properties, as do all the fluoroxyhypo-

molybdates, and is similar in crystalline form to cupric fluoroxy-molybdate.

Cuprous fluoride cannot be prepared by the method given by Berzelius (*Ann. Phys. Chem.*, **1**, 28). The many attempts made by the author to prepare cuprous fluoride in various ways merely gave metallic copper; there is little doubt but that the substance obtained by Berzelius was the impure metal.

Zinc fluoroxyhypomolybdate, $\text{MoOF}_3 \cdot \text{ZnF}_2 \cdot 6\text{H}_2\text{O}$, separates in transparent, blue crystals of vitreous lustre from a solution of zinc oxide (1 mol.) in an electrically reduced solution of molybdic anhydride (1 mol.) in hydrofluoric acid. The crystals rapidly deliquesce in the air, forming a dark blue paste; they belong to the rhombohedral system $a : c = 1 : 0.5136$ or $\xi = 112^\circ 51'$, and present the same crystallographic properties as the corresponding fluorosilicates, fluorostannates, and analogous salts. Tables are given showing the crystallographic resemblances between the above and similar salts.

W. J. P.

Preparation of Tungstates free from Molybdenum. By C. FRIEDHEIM and R. MEYER (*Zeit. anorg. Chem.*, **1**, 76—81).—Commercial tungstates and tungstic acid contain varying quantities of molybdenum. After several unsuccessful attempts to get rid of this impurity, the following method was found to give the desired result. Sodium tungstate, prepared in the usual way, is dissolved in cold water, and to the saturated solution hydrochloric acid is added until the reaction is only feebly alkaline; the paratungstate thus obtained is crystallised out and once recrystallised. One half of it is dissolved in boiling water, and hydrochloric and a little nitric acid added; hydrated tungstic acid is precipitated. This is washed thoroughly with hot water and added to a boiling solution of the other half of the paratungstate, until a portion no longer gives a precipitate with hydrochloric acid. The bulk of the solution is then filtered, hydrochloric acid is added, and the solution is boiled and repeatedly saturated with hydrogen sulphide. This precipitates the molybdenum as sulphide, whilst the metatungstate is not attacked. The solution is filtered, concentrated, oxidised with a few drops of bromine water, and neutralised with soda; pure sodium paratungstate can then be obtained from it by crystallisation. To obtain the potassium and ammonium salts, the acid should be prepared by adding hydrochloric acid to the sodium salt, and then neutralised with potash or ammonia.

An analysis of sodium paratungstate thus prepared agreed better with the formula $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$ than with $3\text{Na}_2\text{O} \cdot 7\text{WO}_3 \cdot 16\text{H}_2\text{O}$.

C. F. B.

Crystallised Sodium Titanates. By H. CORMIMBŒUF (*Compt. rend.*, **115**, 823—825).—The titanates $2\text{Na}_2\text{O} \cdot 3\text{TiO}_2$; $\text{Na}_2\text{O} \cdot 2\text{TiO}_2$, and $\text{Na}_2\text{O} \cdot 3\text{TiO}_2$ are obtained by heating the titanate $3\text{Na}_2\text{O} \cdot 2\text{TiO}_2$, with sodium tungstate containing various proportions of free tungstic acid.

The sesquitanate is obtained in short hyaline or milk-white prisms by heating 5 parts of normal sodium tungstate at 800° for 10 hours with a previously fused mixture of 1 part of titanic anhydride and

2 parts of sodium carbonate. The crystals are optically active, belong to the monoclinic system, and are macled after the manner of feldspars; they are insoluble in water, but dissolve slowly in cold hydrochloric acid and more rapidly on heating.

The bititanate is obtained in imperfect crystals of similar form by heating 20 parts of normal sodium tungstate and 5 parts of tungstic anhydride with a previously fused and finely powdered mixture of 4 parts of titanitic anhydride and 8 parts of sodium carbonate. The crystals are insoluble in water and are very slowly attacked by cold hydrochloric acid, but dissolve rapidly when heated with this acid.

The trititanate is obtained in long, highly birefractive needles by heating 10 parts of normal sodium tungstate and 5 parts of tungstic anhydride with a previously fused mixture of 2 parts of titanitic anhydride and 4 parts of sodium carbonate. It is almost insoluble in boiling hydrochloric acid, and in sulphuric acid it dissolves about as readily as titanitic anhydride.

When the composition of the fused tungstate approaches that of the normal tungstate, rutile separates instead of a titanate. The acid titanates seem unable to take up a further quantity of base, even when fused with highly basic tungstates.

C. H. B.

Action of Antimony on Hydrochloric acid. By A. DITTE and R. METZNER (*Compt. rend.*, 115, 936—939).—Pure antimony, precipitated by tin from an acid solution of the trichloride, does not attack hydrochloric acid of any strength at any manageable temperature, even in the presence of platinum or gold chloride. In the presence of oxygen, however, the metal is slowly dissolved, but the dissolution takes place with equal facility in the absence of the acid.

JN. W.

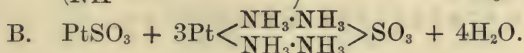
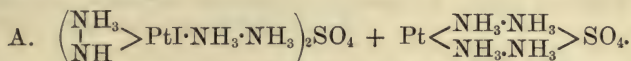
Double Halogen Compounds of Gold. By E. PETERSEN (*J. pr. Chem.* [2], 46, 328—335).—Krüss and Schmidt (*Abstr.*, 1888, 28, 1256) maintain that there are no such compounds as Au_2Cl_4 and Au_2Br_4 , the products of the action of chlorine and bromine on gold being a mixture of unaltered metal with the trichloride and tribromide respectively. The author points out that water or ether, as employed by Krüss and Schmidt, to wash out the trichloride or tribromide is inadmissible, inasmuch as the dichloride and dibromide are decomposed thereby. He uses dry absolute alcohol at -20° as a solvent for any trichloride, and he obtains considerable evidence that even with this the dichloride is being slowly decomposed. The experiments with chlorine were conducted substantially as directed by Thomsen (*Abstr.*, 1888, 559), and they led the author to conclude that by the action of a rapid current of chlorine on finely-divided gold, without the application of external heat but with provision for retaining the heat developed, auroauric chloride, Au_2Cl_4 , together with a small quantity of auric chloride, is formed. This conclusion was confirmed by a thermochemical investigation.

The evidence in favour of Au_2Br_4 was not so good, inasmuch as no solvent for the tribromide could be found which would not decompose the tribromide; but, considered in conjunction with a thermochemical

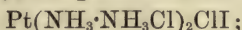
investigation, it was sufficient to justify the author in concluding that aurosoauric bromide also has a separate existence.

A. G. B.

Some Platinum-Ammonium Compounds. By O. CARLGREN and P. T. CLEVE (*Zeit. anorg. Chem.*, **1**, 65—75).—By the action of a boiling solution of sulphurous anhydride on the iodonitrate, $\begin{smallmatrix} \text{NH}_3 \\ | \\ \text{NH} \end{smallmatrix} > \text{PtI} \cdot \text{NH}_3 \cdot \text{NH}_3 \cdot \text{NO}_3$, the following two complex crystalline substances are formed:—



A forms star-shaped groups of ill-defined, colourless or pale yellow crystals. When treated with hydrochloric acid, it yields *platodiamine chloride*, $\text{Pt}(\text{NH}_3 \cdot \text{NH}_3 \cdot \text{Cl})_2$ and *platinodiamine iodochloride*,



the former in colourless needles, the latter in brown crystals. When heated with 3 per cent. hydrogen peroxide, it yields *iodohydroxyplatino-diamine sulphate*, $\text{HO} \cdot \text{PtI} < \begin{smallmatrix} \text{NH}_3 \cdot \text{NH}_3 \\ | \\ \text{NH}_3 \cdot \text{NH}_3 \end{smallmatrix} > \text{SO}_4 + \text{H}_2\text{O}$, and *hydroxy-platinodiamine sulphate*, $\text{Pt}(\text{OH})_2 < \begin{smallmatrix} \text{NH}_3 \cdot \text{NH}_3 \\ | \\ \text{NH}_3 \cdot \text{NH}_3 \end{smallmatrix} > \text{SO}_4 + 4\text{HO}$; the first in small, reddish-brown combinations of the cube with the octahedron, the second in long, colourless needles with inclined end faces, and also crystallised with $1\text{H}_2\text{O}$, in large, colourless plates. When treated with silver nitrate, it yields silver iodide, and a compound $\left(\text{Pt} < \begin{smallmatrix} \text{NH}_3 \cdot \text{NH}_3 \\ | \\ \text{NH}_3 \cdot \text{NH}_3 \cdot \text{NO}_3 \end{smallmatrix} > \right)_2 \text{SO}_4 + \text{Pt} < \begin{smallmatrix} \text{NH}_3 \cdot \text{NH}_3 \\ | \\ \text{NH}_3 \cdot \text{NH}_3 \end{smallmatrix} > \text{SO}_4$, in star-shaped groups of tetragonal plates ($a : c = 1 : 1.0257$).

B, when treated with silver nitrate, yields two crystalline compounds, $\text{PtSO}_3 + 3\text{Ag}_2\text{SO}_3$, and $\text{Pt}(\text{NH}_3 \cdot \text{NH}_3 \cdot \text{Cl})_2$, the first directly, as a white precipitate, the second (platodiamine chloride) when the solution filtered from this precipitate is treated with hydrochloric acid.

The action of hydrogen peroxide on certain compounds was then studied. *Hydroxyplatinodiamine chloride*, $\text{Pt}(\text{OH})_2(\text{NH}_3 \cdot \text{NH}_3 \text{Cl})_2$, was obtained both by decomposing the sulphate with barium chloride and by the action of hydrogen peroxide on platodiamine chloride; it forms small, colourless, tabular, monoclinic crystals, $a : b : c = 1.5310 : 1 : 0.6702$. The *bromide* and *iodide*, with analogous formulæ, were prepared from the sulphate by the action of barium bromide and iodide respectively; the first forms short, colourless prisms with pyramidal end faces, the second tiny, hexagonal prisms. The *nitrite*, $\text{Pt}(\text{OH})_2(\text{NH}_3 \cdot \text{NH}_3 \cdot \text{NO}_2)_2$, was obtained by the action of silver nitrite upon the chloride; it crystallises in needles, and explodes when heated. The *nitrate*, $\text{Pt}(\text{OH})_2(\text{NH}_3 \cdot \text{NH}_3 \cdot \text{NO}_3)_2$, obtained from the sulphate and barium nitrate, or from platodiamine nitrate and hydrogen peroxide,

forms dendritic aggregates of flat, rhombic tables, and explodes when heated. The *sulphate*, $\text{Pt}(\text{OH})_2(\text{NH}_3\cdot\text{NH}_3)_2\text{SO}_4$, was obtained by the action of hydrogen peroxide on platodiamine sulphate, both crystallised with $4\text{H}_2\text{O}$, as described above, and anhydrous in small prisms. The *dichromate*, $\text{Pt}(\text{OH})_2(\text{NH}_3\cdot\text{NH}_3)_2\text{Cr}_2\text{O}_7$, was obtained by the action of hydrogen peroxide on the precipitate formed when potassium dichromate is added to platodiamine chloride. It is a lemon-yellow powder which explodes when heated. C. F. B.

Mineralogical Chemistry.

Vanadiferous Lignite in the Argentine Republic. By J. J. J. KYLE (*Chem. News*, 66, 211—212).—A seam of lustrous, non-fibrous, very brittle, black, bituminous coal has been discovered near the town of San Raphael, province of Mendoza, Argentine Republic. The sp. gr. of the coal is 1.173, and its proximate composition:—

Loss at 100°	2.05
Volatile matters.....	49.51
Fixed carbon.....	47.81
Ash.....	0.63
	100.00

The ash is greenish, and has the following percentage composition:—

Soluble in acid.	Insoluble in acid.	Undetermined.
V_2O_5 38.22	SiO_2 13.70	Traces of Mn,
P_2O_5 0.71	Fe_2O_3 ... 9.42	MgO, Cl, and
SO_3 12.06	Al_2O_3 ... 5.26	loss, 1.33
CaO 8.44	MgO ... 0.83	
Fe_2O_3 ... 4.98		
Al_2O_3 ... 3.32		
K_2O 1.73		

The vanadium is nearly all soluble in alkali, and would seem, therefore, to be present in the ash chiefly as the uncombined pentoxide, partly as potassium vanadate, some, also, as iron or aluminium vanadate; and, inasmuch as a ton of this coal would yield $4\frac{1}{4}$ lbs. of vanadium, it must be regarded as a rich source of vanadium compounds. D. A. L.

Artificial Production of Zircon. By K. v. CHROUSTCHOFF (*Jahrb. f. Min.*, 1892, ii, Mem. 232—236).—The author describes an apparatus he has devised for heating aqueous solutions to a red heat. Unlike that employed by Friedel and Sarasin, which consisted of a steel tube closed at both ends by platinum plates, it is closed at one

end only, and consists of a cylindrical platinum crucible enclosed in a cast-steel block, the lid being screwed down in such a manner as to withstand great pressure. Hitherto but two experiments have been made with this apparatus.

In the first experiment, the crucible was charged with gelatinous silica, gelatinous alumina, and gelatinous zirconium hydroxide. It was subjected to a gradually increasing heat for six days, and allowed to cool. The residue in the crucible was then found to consist of a white powder, in part distinctly crystalline. The crystals exhibited, under the microscope, hexagonal forms, and had a sp. gr. of 2·87. On analysis, they yielded—

SiO ₂ .	Al ₂ O ₃ .	ZrO ₂ .	H ₂ O.	Total.
53·65	23·76	14·54	7·86	99·81

A mineral of this composition is unknown in nature. It may, however, be described as a zirconia-bearing pyrophyllite.

In the second experiment, the crucible was charged with gelatinous silica and gelatinous zirconium hydroxide, and hermetically sealed. It was heated for two hours by 12 bunsen burners. On cooling, it was found that no water had escaped. The crystals obtained were mostly pyramidal, and gave, on analysis, 32·84 per cent. of silica and 67·17 per cent. of zirconia. B. H. B.

Cobaltiferous Chalybite from Neunkirchen. By G. BODLÄNDER (*Jahrb. f. Min.*, 1892, ii, Mem. 236).—A red mineral, occurring in thin layers on quartz at the cobalt mine, near Neunkirchen, in the Siegen district, gave, on analysis, the following results:—

FeO.	CaO.	MgO.	CoO.	CO ₂ .
54·34	1·21	8·80	3·85	41·55

The mineral is thus a spathic iron ore containing isomorphous admixtures of carbonates of calcium, magnesium, and cobalt, its red colour being due to the last named. B. H. B.

Crystallised Slags from Raibl. By P. P. HEBERDEY (*Zeit. Kryst. Min.*, 21, 56—73).—The author has made a chemical and crystallographical examination of a series of slags from the Raibl lead works, collected for the University of Vienna. The results are of interest in that an artificial lead zinc chrysolite has been observed, the existence of which has hitherto been unknown. Analysis shows this mineral to have the formula $Pb_{10}Zn_7Mg_2FeSi_{10}O_{40}$.

In an appendix to the paper, the author gives analyses of the dolomite in which the Raibl galena deposits occur. In this dolomite, he has detected distinct traces of thallium and of lithium.

B. H. B.

Artificial Production of Garnet (Melanite) and Spheue. By L. MICHEL (*Compt. rend.*, 115, 830—832).—An intimate mixture of 10 parts of titaniferous iron ore, 10 parts of calcium sulphide, 8 parts of silica, and 2 parts of carbon was heated in a graphite crucible at a

temperature of 1200° for about five hours, and allowed to cool very slowly. The lower part of the regulus consists of the iron sulphide Fe_4S_3 , with some granules of iron carbide; the upper part is of porous texture, and contains vesicles which enclose crystals of garnet (melanite), sphene, and the iron sulphide.

The garnet is obtained in rhomboidal dodecahedra about 0.5 mm. in diameter; hardness 7; sp. gr. 3.8. They are dark brown with a vitreous lustre, melt to a black magnetic glass, and have the composition SiO_2 , 36.45; Fe_2O_3 , 29.80; and CaO , 32.65 = 98.90.

The artificial sphene forms translucent, monoclinic prisms, elongated along $h'g'$ or (100)(010), the angle mm or (110)($1\bar{1}0$) being $113^{\circ} 26'$, whilst that of the natural crystals is $113^{\circ} 31'$. They attain a length of 4 mm., have a strong, positive birefracton with the plane of the optical axes in g' , a reddish-brown colour, and an adamantine lustre; hardness 5; sp. gr. 3.4. Their composition is SiO_2 , 32.10; TiO_2 , 40.00; CaO , 27.14; Fe_2O_3 , traces = 99.24.

Both garnet and sphene have previously been obtained artificially, but never by this method, and in one operation.

The iron sulphide Fe_4S_3 was obtained in small crystals which seemed to belong to the rhombic system, and were identical in their properties with those obtained by Gautier and Hallopeau (Abstr., 1889, 677).

C. H. B.

Friedelite from the Sjö Mine, Sweden. By L. J. IGELSTRÖM (*Zeit. Kryst. Min.*, 21, 92—95).—Friedelite has been found by the author at the Sjö mine, Örebro, Sweden, in association with hausmannite and braunite. An analysis of the mineral gave the following results:—

SiO_2 .	Cl.	MnO.	FeO.	CaO.	MgO.	Mn.	H_2O .	Total.
34.36	3.00	45.88	1.35	1.50	1.50	2.79	9.00	99.38

The results are in perfect accord with those of analyses of friedelite from Adervielle, in the Pyrenees, and from Harstigen, in Sweden, the two other localities at which this interesting mineral has been observed.

B. H. B.

Minerals of the Pyroxene Group. By A. SCHMIDT (*Zeit. Kryst. Min.*, 21, 1—55).—In this lengthy paper, the author gives the results of a careful crystallographical investigation of the members of the monosymmetrical series of the pyroxene group which are usually known as diopsides. His researches were conducted with the following minerals:—Diopside from the Ala Valley, the white and green diopsides from Achmatowsk, the diopsides from Nordmarken and from the Ziller Valley, and, lastly, the augites of the Arany Mountains.

B. H. B.

Chemical Constitution of Hornblende. By H. HAEFCKE (*Jahrb. f. Min.*, 1892, ii, Ref. 404—406).—The author has analysed eight specimens of hornblende, all of which were found to contain alkalis. According as they are free from sesquioxides or not, they

appear to be isomorphous mixtures of bisilicates or of normal silicates. In almost all cases the results were influenced by the presence of large amounts of mica in the hornblendes examined, so that the existence of hornblende formed exclusively from normal silicates is still open to question.

B. H. B.

Physiological Chemistry.

Influence of Light on Gas Exchange. By C. A. EWALD (*J. Physiol.*, 13, 847—859).—Taking the average of 17 experiments, the carbonic anhydride excreted by curarised frogs in the light exceeds that produced in the dark by less than 2 per cent., the ratio being 100 : 98·5. If two series are thrown out, where slight muscular movements occurred, the animals being incompletely under the influence of the drug, the ratio of the remaining 15 is 100 : 99, a difference which comes within experimental error. Muscular action being eliminated, light does not in any appreciable way influence the excretion of carbonic anhydride.

W. D. H.

Gaseous Tension in the Blood and Serum of Peptonised Animals. By V. GRANDIS (*Real. Accad. Linc.*, 7, ii, 471—478).—By the peptonisation of animals, the blood acquires the property of giving up a larger quantity of carbonic anhydride than usual in its passage through the lungs. The gaseous tension and other properties of the blood were examined in Gaule's apparatus, and in order to ensure absence of oxygen, the blood was drawn from the asphyxiated animal; the gas obtained in this way consisted principally of carbonic anhydride mixed with a little nitrogen. Comparative experiments were made on dogs both before and after injection of the peptone solution. It was found that blood drawn from the right auricle has a greater gaseous tension than normal blood from the same source; the reverse is true of blood drawn from the carotid.

Experiments on the amount of free and combined carbonic anhydride in the serum of peptonised blood, show that the former is slightly greater than in the normal blood serum; the quantity of combined carbonic anhydride in the serum is considerably diminished by peptonisation. Tables are given supporting the author's conclusions.

W. J. P.

Elimination of Carbonic Oxide. By L. DE SAINT-MARTIN (*Compt. rend.*, 115, 835—839).—Rabbits were allowed to breathe for 15 to 20 minutes, through a canula inserted in the trachea, a mixture of 2 litres of oxygen with 70 c.c. of carbonic oxide, and the quantity of oxygen absorbed was determined by analysis of the gas remaining in the flexible india-rubber bag in which the original mixture was contained. The rabbits were then allowed to breathe pure oxygen, the exhaled gas being all collected, and the carbonic oxide in it estimated.

The elimination is at first very rapid, but quickly diminishes, becoming very slight at the end of the third hour. From 5 to 6 per cent. of the absorbed carbonic oxide is, however, never eliminated as such, but undergoes alteration in the living tissues, and is probably converted into carbonic anhydride. C. H. B.

Influence of Increased or Diminished Consumption of Food and of the Salts added to the Food, on Digestion and Resorption. By H. WEISKE (*Landw. Versuchs-Stat.*, **41**, 145—164).—In order to ascertain the power of digestion and resorption for oats, the solid excrement of five of the rabbits used in the last experiment (*Abstr.*, 1892, 647), namely, *K* (fed with oats alone), *M* (fed with oats and calcium phosphate), *J* (oats and sodium hydrogen phosphate), *O* and *N* (oats and sodium citrate), was collected for sixteen successive days, weighed, and analysed. The amount of protein differed considerably, being least in *K* and *M* (4.75 and 5.25 per cent.), and highest in *O*, *N*, and *J* (10.81 per cent.). *J* gave also the highest amount of ether extract (4.07), *N* and *O* the least (1.74 and 1.55 per cent.). The amounts of substance soluble in warm water and in artificial gastric juice were also determined: the amount of soluble substance (in water) was nearly twice as much in the case of the excrement from *J* as in the others, whilst the substance soluble in gastric juice was much greater in *N* and *O* than in *K* and *M*. The amount of food consumed by the five rabbits during the experiment was about equal, amounting (for the 16 days) to 884—890 grams of air-dry oats. For *M*, the food was about sufficient, whilst all the others lost weight, *K* 125, *J* 540, *N* 885, and *O* 300 grams, in three months. When the results with *K* (which had no salts) are compared with an earlier experiment (*Landw. Jahrb.*, **21**, 796), in which the rabbit was similarly fed, except that it had 100 grams of oats daily, instead of 55.5 grams, as in these experiments, a great difference is found in the digestion coefficients (except ether extract), indicating that with the same foods the amounts digested are much less when large amounts of food are consumed. Tables are given showing the digestion coefficients obtained with the five rabbits; there are differences, but they are not great, and are, moreover, irregular, except as regards the protein, which is highest in the case of *K*, the next highest being *M*, whilst *J*, *N*, and *O* differ most from *K*.

A fresh series of experiments was made, in which five rabbits, about seven months old, were fed with oats, *ad libitum*; four of them, Nos. 2—5, having, respectively, each day, 0.1, 0.25, 0.5, and 0.75 gram of sodium citrate; No. 1 having none. Each of the rabbits consumed 1 kilo. of oats in 10 days, after which their appetites began to fail, especially in the case of 4 and 5. Tables are given showing the amounts of oats consumed during the whole period of 49 days, the increase of weight, and the weight and composition of the excrement of each rabbit. The digestion coefficients show only slight differences, as if the addition of sodium citrate had been without effect. But when the amounts of food consumed daily are considered, it is seen that the presence of citrate in Experiments 2—5 caused an

increasing diminution in the amount of food consumed, and that instead of the food being more completely digested, as the amount diminished (as was observed when different amounts of oats, both without salts, were consumed), the using up of the food was the same.

An examination of the blood of the rabbits at the end of the experiment gave the following results:—No. 1 contained 5.78 per cent., No. 5, 5.90 per cent. of ash. The ash contained—

	K ₂ O per cent.	Na ₂ O per cent.	CaO per cent.
1.	21.68	38.24	1.14
5.	18.63	35.65	0.68

results which agree with those of W. Beckmann, who found that sodium citrate had the power of withdrawing sodium and potassium, &c., from the body. N. H. M.

Proteïds of Kidney and Liver Cells. By W. D. HALLIBURTON (*J. Physiol.*, 13, 806—846).—Contrasting the proteïds found in the liver and kidney with those found in the simpler animal cells, such as lymph cells (*Abstr.*, 1888, 974), the following general conclusions are arrived at:—

1. Albumin is either absent (kidney) or present in the merest traces (liver, lymph cells).

2. The proteïds present fall into two classes; nucleo-albumins and globulins.

3. The nucleo-albumin of lymph cells, and of the kidney, is obtainable by two methods: (a.) The finely-divided organ is extracted with distilled water for 24 hours, and this solution precipitated by weak acetic acid. The substance so obtained, called "tissue fibrogen," by Wooldridge, is a mixture or loose compound of nucleo-albumin with lecithin. (b.) The finely-divided organ is ground up in a mortar with sodium chloride, and the resulting viscous mass poured into excess of distilled water. The nucleo-albumin rises to the surface of the water. That the material prepared by the two methods is identical is shown by—

i. The result of gastric digestion, leading to an insoluble residue of nucleïn. ii. After extraction of the organ by one method, the residue yields only traces by the other. iii. The heat coagulation temperature is the same, namely, 63—65°, in the case of the kidney. iv. Phosphorus estimation in both cases gives the same result; in the case of the kidney 0.37 per cent.

4. The liver nucleo-albumin is obtainable in small quantities only, and only by the first method just described; it is remarkable for its high percentage of phosphorus, 1.45 per cent.

5. All these produce intravascular clotting when injected into the circulation in rabbits. They do so even after the removal of the lecithin. This may be because nucleo-albumin is the mother substance of fibrin ferment (*Pekelharing, Abstr.*, 1892, 1112); or partly because these substances dissolve the white corpuscles.

6. The nucleo-albumins give none of the reactions of a proteose or peptone (compare *Wright, Abstr.*, 1892, 646).

7. In all these varieties of cells there is a globulin which is coagulated by heat at about 48—50°. There is, in addition to this, in the liver cells, a globulin, which is coagulated by heat at about 70°.

8. Peptone, proteose, pepsin, myosin, and mucin are absent from both liver and kidney cells.

9. The proteid formerly called cell-globulin β by the author is a nucleo-albumin, although whether it is the same as, or different from, that already mentioned, must be subject of renewed research.

10. Liver and kidney, when fresh and blood-free, have an alkaline reaction. Like muscle and lymph cells, they turn acid in a short time.

W. D. H.

Mucin in Bone. By R. A. YOUNG (*J. Physiol.*, **13**, 803—805).—Ebner (*Arch. milr. Anat.*, **29**) having shown the close analogy of the decussating fibres in bone to the white fibres of connective tissue, and that they are not calcified, it appeared necessary to investigate whether the matrix in which they are imbedded is completely calcified or not. This question may be most readily solved by ascertaining whether mucin, the most abundant constituent of the uncalcified matrix of connective tissue, is present or absent. The dense compact tissue of bone was used (care being taken to strip off all the periosteum), and not the spongy bone, as it is very difficult to free the latter from admixture with marrow, and it has been shown by Rustitzky (*Centr. med. Wiss.*, 1872, 562) that the marrow of some bones yields mucin. The bone was used either in the form of fine shavings or in powder, and was covered with excess of lime water or baryta water (diluted with 4 parts of water). The mixture was left for three or four days (being frequently stirred), and then filtered. The filtrate was treated with acetic acid of various strengths, but in no case was there any precipitate. Thus, ordinary compact bone, unlike the other connective tissues, contains no mucin, and from this it appears that in the process of ossification the connective tissue matrix is completely calcified.

W. D. H.

Lacto-globulin. By R. T. HEWLETT (*J. Physiol.*, **13**, 798—802).—Sebelien stated that ordinary cows' milk contains a small quantity of globulin (precipitable by saturation with magnesium sulphate after the caseinogen has been precipitated by saturation with sodium chloride).

Halliburton (*Abstr.*, 1891, 339) found that this precipitate does occur, but considered it to be a portion of the lactalbumin precipitated by the saturation with two salts.

Sebelien (*Abstr.*, 1901, 951) having reaffirmed his original statements, the present research was undertaken to test their accuracy. The following conclusions are arrived at:—

1. Sodium chloride is a more perfect precipitant of caseinogen than magnesium sulphate.

2. Caseinogen in milk is not completely precipitated by saturation with either sodium chloride or magnesium sulphate, a small quantity

remaining in solution, and this is precipitable by warming to 35°, or by saturation with a second neutral salt.

3. This residual caseinogen is, possibly, more intimately associated with the calcium salts in milk than the rest of the caseinogen, as the precipitate is found to be mixed with a considerable quantity of calcium sulphate; this is more abundant when the milk is first saturated with magnesium sulphate, and then with sodium chloride.

4. This residual caseinogen forms the greater part of Sebelien's lacto-globulin; there is, however, a very small quantity of a true globulin present; it is precipitated by dialysis, and by saturation with neutral salts, coagulable by heat, and not by rennet.

5. In order to prepare pure lacto-albumin, it is necessary to dialyse its solution for some time to precipitate remaining traces of caseinogen and globulin.

W. D. H.

Microchemical Localisation of Phosphorus in the Tissues.

By L. LILIENFELD and A. MONTI (*Zeit. physiol. Chem.*, 17, 410—424).

—The importance of phosphorus in bio-chemistry is very great: for not only inorganic phosphates occur, but organic compounds like lecithin, protagon, and nucleïn.

The method recommended for detecting this element, microchemically, in the tissues is the following:—

The organ or tissue must be fresh; the preparation is placed in a solution of ammonium molybdate, and is left there for minutes or hours, according as to whether the phosphorus is in a simple or complex union. The pieces of tissue, which appear yellow to the eye if much phosphorus is present, are then washed with water containing a little pyrogallol, until the liquid no longer takes a brown-yellow tint, but remains clear. The pieces are then placed in 20 per cent. pyrogallol; this reduces the phosphomolybdic acid, and leads to yellow, brown, or black coloration, according to the amount of phosphorus present. After a few minutes, the preparation is again washed, and examined microscopically in water, or it may be passed through alcohol into xylene, and mounted in balsam.

For sections, the following modification is recommended:—The sections are taken directly from the molybdate to an ethereal solution of pyrogallol. The coloration is not so diffused as when water is used in washing.

The method was found to give good results with substances like nucleïc acid rich in phosphorus, whilst it gave negative results with proteïds free from phosphorus. It was then applied to cells and tissues with the following results:—

1. Cells in general. The nucleus is deeply coloured, especially the karyomicrosomes, and the optical sections of the nuclear network. The protoplasm is coloured also, but less intensely. In cell division, it is the chromatic fibres which are most stained. This, however, was in vegetable cells. In the cells of the testis, the protoplasm is so rich in phosphorus that hardly any distinction between it and the nucleus could be made out. The cell membrane of plant cells is not coloured; the crystals of plant vitellin are deeply coloured.

2. Bacteria are coloured a weak brown.

3. Epithelial cells of the frog and salamander's epidermis.—The nucleus is coloured; in the deeper layers the cytoplasm is coloured also, but less deeply; on the surface, when mucin is being formed, it is not coloured.

4. Hydra.—Here also the nuclei are better stained than the protoplasm.

5. Spermatozoa.—The head is intensely coloured; the rest not. In dog's spermatozoa the hinder part of the head is most coloured.

6. Blood.—The red corpuscles are stained a deep yellow-brown, due probably to lecithin. The leucocytes behave like other cells; their nucleus is darkly, their cytoplasm faintly, coloured. The platelets are dark brown.

7. Connective tissues.—Here the nuclei of the cells stand out prominently.

8. Bone.—The large amount of phosphates here rendered the observations valueless.

9. Cartilage.—The matrix is free from phosphorus; the cells contain it, especially their nuclei.

10. Nerve cells.—Here the nuclei are less coloured than the cytoplasm.

11. Kidneys.—The whole cytoplasm is rich in phosphorus; this is probably due to phosphates passing into the urine.

12. Muscle.—The deep colour readily produced here is also probably due to phosphates. The coloration is most marked in the dark stripes.

W. D. H.

Lactic acid in Blood and Urine. By T. IRISAWA (*Zeit. physiol. Chem.*, 17, 340—352).—The results of this research may be summed up as follows:—

1. Lactic acid is always present in blood removed from the dead body.

2. In urine drawn off from men shortly before death, lactic acid was found three times in seven cases.

3. The presence of lactic acid in blood corpuscles and pus was also noted.

4. In blood drawn freshly from the veins of a dog, lactic acid was found in each experiment.

5. In artificially produced anæmia, the amount of lactic acid in the blood rises in proportion to the lessening of oxidation processes.

Crystals of potassium dihydrogen phosphate were prepared from liver and pancreas; the acidity of dead organs is probably partly explicable in this way.

W. D. H.

Action of Phosphorus and of Arsenious Anhydride on the Animal Organism. By T. ARAKI (*Zeit. physiol. Chem.*, 17, 311—339).—In previous researches (Abstr., 1891, 1125, 1392; 1892, 517, 1113) it has been shown that various circumstances tending to a diminution of oxidation processes in the body lead to the appearance of lactic acid in the urine; the present communication is a continuation of these, the experiments being performed on dogs and rabbits. The phosphorus was administered dissolved in olive oil, subcutaneously;

the arsenious anhydride was mixed with the food. In the case of phosphorus poisoning, lactic acid appears quickly after the poison is given; the amount varies, and the variations show no relation to the liver affection produced. The amount of lactic acid in the urine may be increased by combining carbonic oxide poisoning with that produced by phosphorus. Jaundice sets in later; it is almost entirely bile pigment only that passes into the urine.

The appearance of lactic acid in the urine cannot be explained on the grounds of anæmia. The amount of blood pigment varies but little. It is probably due to the diminished activity of the heart, and thus indirectly to a lessening of oxidation processes by the slowing of the circulation through the lungs and tissues.

Glucose is seldom formed in the urine, thus contrasting with carbonic oxide poisoning. Leucine and tyrosine were never found.

The action of arsenious acid is precisely similar, only rather slower in onset.

W. D. H.

Putrefaction in the Intestines. By C. SCHMITZ (*Zeit. physiol. Chem.*, 17, 401—403).—Rovighi (*Abstr.*, 1892, 226), Winternitz (*ibid.*, 1116), and others have stated that a diet of milk or kephir lessens the ethereal hydrogen sulphates in the urine. This has been ascribed to the lactic acid produced from the milk sugar acting as an antiseptic in the intestines.

The present communication states :—

1. That feeding with lactose, mixed with the ordinary diet, causes no lessening of the output of ethereal hydrogen sulphates.

2. Administration of free hydrochloric acid with the food causes, in dogs, no lessening of the ethereal hydrogen sulphates in the urine.

3. In man, however, 40 or 50 drops of a 10 per cent. solution of hydrochloric acid, given in the day, lessen the output of these sulphates by as much as 40 per cent. This is in accordance with the observations of Biernacki (*Deut. Arch. klin. Med.*, 49, Heft 1).

4. The constituent of milk and kephir, which produces the lessening in the output of these sulphates is casein. Feeding dogs on freshly precipitated casein produces this result.

W. D. H.

Ptomaines from the Urine in Erysipelas and Puerperal Fever. By A. B. GRIFFITHS (*Compt. rend.*, 115, 667—669).—See this vol., i, 183.

Chemistry of Vegetable Physiology and Agriculture.

Interchange of Carbonic Anhydride and Oxygen between Plants and the Atmosphere. By T. SCHLOESING, Jun. (*Compt. rend.*, 115, 881—883).—The plants were grown in sealed vessels in a soil of quartz sand mixed with a little chalk, and were watered with

fertilising solution. The uppermost layer of the soil was ignited to prevent the growth of algæ, but even then a blank experiment showed that a slight amount of carbonic anhydride was absorbed, and oxygen evolved.

After the seeds were sown, the air was exhausted from the vessel and replaced by known quantities of pure nitrogen and oxygen, and during the growth, the composition of this atmosphere, small samples of which were withdrawn and analysed from time to time, was adjusted by adding known quantities of carbonic anhydride, or removing known quantities of oxygen by circulation over a known weight of red-hot copper. The total volume of the gas was again measured at the end of the experiment.

Plants of large-leaved cress from 0.0437 gram of seed absorbed in 47 days from the sowing at the end of April, 1171.5 c.c. of carbonic anhydride, and gave out 1563.4 c.c. of oxygen, or in the ratio of 0.75 : 1. Plants of feather-grass (*houque laineuse*) from 0.05 gram of seed absorbed in 43 days, 1501 c.c. of carbonic anhydride, and gave out 1836 c.c. of oxygen, or in the ratio of 0.82 : 1. JN. W.

Absorption of Free Nitrogen by Plants. By T. SCHLOESING, Jun., and E. LAURENT (*Compt. rend.*, 115, 732—735; DUCLAUX, *ibid.*, 735—736; and BERTHELOT, *ibid.*, 737—738).—Schloesing and Laurent have investigated, by the methods previously described, the absorption of free nitrogen by soils on which are growing various algæ, the precise nature of the algæ being determined by Bornet. With cultivations of *Nostoc punctiforme*, *N. minutum*, *Brachythechium rutabulum*, and *Barbula muralis*, in some cases separate, in others mixed in pairs, the absorption of atmospheric nitrogen was very distinct, but no such absorption was observed with cultivations of the similar alga *Microcoleus vaginatus*. Estimation of the carbon and nitrogen in the superficial layer of the soil indicates that the nitrogen absorbed is found in the tissues of the plants, the energy required being provided through the medium of the chlorophyll.

It follows that the absorption of atmospheric nitrogen is effected by the lower vegetable organisms at the surface of the soil, and not, as Berthelot supposes, through the influence of microbes in the body of the soil.

Duclaux, at whose suggestion Schloesing and Laurent undertook these investigations, points out that the occurrence of algæ and lower organisms at the surface of the soil had frequently been observed by Berthelot and others, but that their true function had been overlooked.

Berthelot points out that in one of his earlier papers he showed that the absorption takes place both at the surface of the soil and throughout the mass, and he contends that, although Schloesing and Laurent have proved that certain algæ and other lower organisms containing chlorophyll have the power of absorbing free nitrogen, they have advanced no evidence that this power is not also shared by colourless lower organisms which seem to contain no chlorophyll (as in his own experiments with humic acid) and which occur below the surface of the soil.

C. H. B.

Colouring Matter of Pollen. By G. BERTRAND and G. POIRAULT (*Compt. rend.*, **115**, 828—830).—Yellow and orange pollen from various flowers, with the exception of dry pollen, such as that of *Urticæ*, *Gramineæ*, and the like, contain carotene, which can be extracted with light petroleum, and is identical with the carotene from other sources. Colorimetric estimation indicates that the oily drops on the surface of the pollen of *Verbascum thapsiforme* contain not less than 6·6 per cent. of carotene, which is a relatively high proportion. The carotene occurs in the oily drops that cover the surface of the pollen grains, and it is not improbable that the odour of the product of the spontaneous oxidation of the carotene is attractive to insects.

C. H. B.

Carbohydrates in Leguminous Seeds. By E. SCHULZE (*Landw. Versuchs-Stat.*, **41**, 207—229).—It is probable that β -galactan is present in the seeds of *Pisum sativum*, *Vicia sativa*, and *V. faba*, and that paragalactan occurs in *Pisum sativum*, *Vicia faba*, and in *Soja hispida*, although both have hitherto been prepared from the seeds of *Lupinus luteus*.

β -Galactan (lupeose, Abstr., 1892, 1171) gives no precipitate with sodium, ammonium, and magnesium sulphates, and with ammonium phosphate, and is therefore, perhaps, not a colloïd substance (compare G. Pohl, *Zeit. physiol. Chem.*, **14**, 154). On the other hand, all attempts to obtain it in a crystalline form failed. In this respect, it differs from stachyose, as well as in its behaviour towards strontium hydroxide which precipitates β -galactan and towards hot dilute sulphuric acid. Whilst stachyose yields galactose, grape sugar, and fruit sugar, β -galactan yields galactose, fruit sugar, and at least one other glucose, but no grape sugar. The formula of β -galactan is probably $C_{24}H_{44}O_{22}$ or $C_{36}H_{60}O_{33}$. The amount of β -galactan in lupin seeds was estimated (*Landw. Versuchs-Stat.*, **39**, 283) by boiling an aqueous extract with dilute hydrochloric acid, extracting the glucose, and calculating the amount of β -galactan, on the assumption that 100 parts of β -galactan yield 111 parts of glucose: a percentage of 10·20 was found. Inasmuch as fruit sugar is also found, it is obvious that the result was too low; in fact only about 80 per cent. of the theoretical amount of glucose is actually produced. The percentage of β -galactan would thus be 12·75 (instead of 10·20). Almost the same results (13·12 and 12·44) were obtained with other samples of seeds by comparing the results obtained from the aqueous extracts with that obtained with β -galactan itself. Another determination by means of the amount of mucic acid obtained by oxidation with nitric acid, gave the percentage 11·2. The results indicate that β -galactan is the only soluble carbohydrate which occurs in lupin seeds in any quantity.

When paragalactan is hydrolysed, arabinose is formed as well as galactose, and it is suggested that the name of paragalactan should be altered to *paragalactoaraban*. It was already shown (*Landw. Versuchs-Stat.*, **36**, 447) that this substance is very easily altered by acids, and it seemed desirable to examine the behaviour of the substance towards Hoffmeister's reagents for cellulose (*Landw. Jahrb.*, **17**, 239). For this purpose, the residue obtained by extracting finely-

powdered lupin seeds with ether, then with dilute aqueous potash, and finally with water, was employed. This residue contained crude protein (3·38), non-nitrogenous substance (85·72), and ash (10·90 per cent.). When treated successively with a mixture of hydrochloric acid and potassium chlorate, and with hot, dilute ammonia, an average amount of 25·71 per cent. of cellulose was obtained (30 per cent. of the non-nitrogenous constituents of the residue). Glacial acetic acid at 90° (Hoffmeister's method for removing starch, *Landw. Jahrb.*, 18, 774) dissolves the greater part of the residue, which is thus scarcely more stable than starch (compare Abstr., 1890, 284).

N. H. M.

Amount of Ash in Etiolated Leaves. By W. PALLADIN (*Expt. Stat. Record*, 4, 207; from *Ber. deut. bot. Ges.*, 1892, 179).—Etiolated leaves of wheat and vetch were found to contain less ash than the green leaves; the difference was specially marked in the case of the calcium. A similar diminution of ash was observed with plants grown in air kept saturated with moisture, that is, with hindered transpiration. This, in conjunction with the fact that the conditions of etiolation hindered transpiration, indicates a connection between transpiration and the acquisition of ash constituents.

N. H. M.

Analyses of California Prunes, Apricots, and Peaches. By G. E. COLBY and H. P. DYER (*Exp. Stat. Record*, 4, 157—162; from *Californ. Bul.*, No. 97, 1892).—The following analytical results, obtained with the various fruits, are given:—

	In fresh fruit (per cent.).				In juice (per cent.).	
	Dry matter.	Ash.	Nitrogen.	Sugar.	Sugar.	Acid (as SO ₃).
Peaches (1)	21·50	0·62	—	15·00	20·00	0·17
Peaches (2)	13·50	0·44	—	10·00	14·00	0·32
Prunes	18·71	0·40	0·148	11·65	16·70	0·43
Apricots	14·43	0·52	0·229	10·76	13·34	0·63
Dried prunes	72·00	1·65	—	47·25	—	0·62

The percentage composition of the pure ash of the whole fruit of (i) French prunes and (ii) Royal apricots is next given.

	K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	MnO ₂ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
I. 65·92	3·18	3·24	6·16	0·85	0·31	15·19	2·37	4·56	0·19	
II. 54·88	10·57	3·52	3·85	1·71	0·31	13·86	2·95	7·85	0·60	

After grapes, apricots remove most mineral matter from the soil; prunes and oranges taking, about equally, the third place. This is contrary to results obtained with European fruits. A table is given showing the amounts of ash, potash, phosphoric acid, and nitrogen in 1000 lbs. of the European and Californian fruits. Whilst Californian

prunes withdraw less mineral, they take up more nitrogen than the European. With regard to apricots, the Californian and European contain about the same amounts of mineral matter, but the former take 2·5 times as much nitrogen as the latter. N. H. M.

Relative Value of Maize Silage and Field and Fodder Maize for Milk and Butter Production. By L. W. WOLL (*Exp. Stat. Record.*, 4, 187—180; from *Wiscon. Stat. Rep.*, 1891, 49—60).—Twenty cows were divided into two lots, which were fed alternately on silage and fodder *ad libitum* in conjunction with hay (4 lbs.), wheat bran (5 lbs.), and wheat shorts (2 lbs.). The first period of the experiment was from December 15 to February 9; the second, February 16 to April 13; each being preceded by a week of preliminary feeding. The weight of milk was recorded each milking, and every three or four weeks the morning and evening milk of each cow was tested by the Babcock method for a week. At such times the cows were weighed daily, and the amount of water consumed ascertained. The total food consumed at each feeding and the amounts left over were recorded. During the silage period, it was found that the average weight of cows was greater than when fed with fodder. The total amounts of milk produced with silage and fodder maize were almost identical, but when the areas of land required to produce the two foods are considered, it is seen that silage would have produced 243 lbs. more milk (or 12 lbs. of butter) than the dry fodder, equivalent to a gain of a little more than 3 per cent. in favour of the silage. N. H. M.

Losses in ensiling and field-curing Maize. By F. W. WOLL (*Exp. Stat. Record.*, 4, 145—147; from *Wiscon. Stat. Rep.*, 1891, 227—231).—129,014 lbs. of maize was put into a silo with 3800 lbs. of millet as a covering. The silage was good with the exception of the top 6 inches. The same weight of maize was left in the field for the greater part of the winter, which was favourable, although the autumn was wet. The maize contained in each case 32,432 lbs. of dry matter and 2580·5 lbs. of protein. Of this the silage lost 10·3 per cent. of dry matter and 12·5 per cent. of protein; whilst the field-cured maize lost 28·3 per cent. of dry matter and 34·8 per cent. of protein. In previous years, the loss in the ensilage was greater, which was probably due to the small quantity of fodder employed. N. H. M.

Influence of the Distribution of Manures in the Soil on their Utilisation. By T. SCHLOESING (*Compt. rend.*, 115, 698—703 and 768—771).—A poor soil prepared by mixing 84 parts of a very sandy subsoil with 16 parts of an argillaceous subsoil was mixed with potassium sulphate, sodium nitrate, superphosphate from bones, and magnesium sulphate. In the first case, the manures were dissolved in water and every care was taken to mix them as uniformly with the soil as possible. In the second case, the soil, which measured 1·75 m. in length, 1·2 m. in breadth, and 0·35 m. in thickness, was cut into eight longitudinal furrows, 12 cm. deep and 15 cm. apart, and one eighth of the mixed manure was spread along the bottom of each

furrow, the furrows being afterwards filled up. In both cases the soil was previously mixed with about 0.25 per cent. of chopped straw in place of humus.

Each quantity of soil was divided into five sections, and wheat, potatoes, beet, haricots, and peas were sown on separate sections. The experiments with beet gave no results in consequence of the attacks of insects and fungi. Wheat, potatoes, haricots, and peas developed somewhat more vigorously in the second case, where the distribution of the manure was irregular, but reached maturity somewhat later, the differences in the time of ripening being least in the case of wheat.

Wheat, haricots, and potatoes gave a distinctly larger crop with an irregular than with a uniform distribution of manure, whilst peas gave practically the same weight of crop under both conditions. The first three plants also utilised a distinctly larger proportion of phosphoric acid when the manure was irregularly distributed, whereas with peas the reverse was the case, probably because the plant developed before the phosphoric acid had time to diffuse through the soil. All four crops utilised a markedly higher proportion of nitrogen when the distribution was irregular, and haricots, peas, and potatoes utilised a considerably higher proportion of potassium. Wheat utilised a somewhat lower proportion of potassium when the distribution was irregular. If the crops in the second case (irregular distribution) had been allowed to ripen fully instead of being cut when the crops in the first case (uniform distribution) were ready, the differences would have been still greater in favour of the second case.

It would seem that, so far as these experiments go, the manures experimented with are better utilised by crops when distributed in lines than when uniformly diffused through the soil. In the former case, a certain number only of the rootlets come in contact with the manure, but meet with it in a concentrated form, whereas in the latter all the rootlets are alike in contact with the manure but the manure is, so to speak, in a much more diluted form. C. H. B.

Employment of Ferrous Sulphate in Agriculture. By H. BOIRET and G. PATUREL (*Ann. Agron.*, 18, 418—440).—After remarking on the conflicting nature of the evidence as to the benefit or injury to crops to be derived from dressings of ferrous sulphate, the authors give a historical sketch of our knowledge on the question and follow this by detailed accounts of recent experiments executed by themselves at Grignon.

Pyritous shales have been long employed in the districts in which they are found. As at first extracted they contain, according to Lefebvre's analysis: iron sulphide, 19.4; carbonaceous matter, 22.5; clay, 34.0; calcium sulphate, 1.9; water, 22.2. Nitrogen is present to the extent of 0.5 to 1.0 per cent. These shales are used as manures after 15—18 months exposure to air, when most of the sulphide is transformed into iron and aluminium sulphates. An instance is given, from experiments made in 1777, where a small dressing of this material (about 850 litres per hectare) more than doubled the

yield of sainfoin as compared with an unmanured plot, and produced a greater increase than a good dressing of farmyard manure. The nitrogen in this dressing would be insignificant; leguminous crops show the greatest benefit from this application. Sir H. Davy's opinion, in commenting on the results obtained with ferrous sulphate by Pearson, was that this substance acted by producing gypsum, and on the same theory he explained its injurious action when lime is lacking in the soil. Gris and Dumont, in France, and Griffiths, in England, have since noticed the deepening of the green tint in chlorotic plants after a very small dressing of ferrous sulphate, and Griffiths has obtained some remarkable increases of crop by employing the salt at the rate of $\frac{1}{2}$ cwt. per acre, in the case of beans, turnips, potatoes, hay, and mangolds, but not with cereals. He maintains that the dressing greatly increases the proportion of iron and of phosphoric acid in the ash of the crops, but diminishes the potash. The author's experiments were as follows:—

Action of Solutions of Ferrous Sulphate on Plants.—Seedlings of peas and oats were supported with their roots immersed in solutions of ferrous sulphate and other salts of known strengths. After a month of immersion in pure water and in sodium nitrate, ammonium sulphate, sodium chloride, or magnesium sulphate solution (2:1000), the plants were healthy and growing; less healthy in the same saline solutions at 5:1000. In ferrous sulphate, lead acetate, copper sulphate, or zinc sulphate, of either strength they were absolutely dead. Experiments with more dilute solutions of ferrous sulphate showed that whilst dilutions of 1/1000 and 1/2000 were still very injurious, a certain amount of growth was possible in dilutions of 1/4000, especially where some of the iron was deposited by oxidation as basic ferric sulphate. During this oxidation free sulphuric acid is formed, which is very deleterious to plants, solutions of 1/5000 being fatal; but in an extremely dilute solution it may be neutralised by calcareous dust from the air. In every case where the solutions of ferrous sulphate became perceptibly acid by oxidation, the plants were killed or injured. Solutions of iron citrate and citric acid are as injurious as those of iron sulphate and sulphuric acid.

Cultures in Artificial Soils containing known proportions of Calcium Carbonate.—The general result of these experiments is that ferrous sulphate is always injurious if the soil does not contain an excess of lime. Directly the drainage water shows traces of free acid, or of soluble iron compounds, injury is perceived. Should these soluble compounds get washed down into a lower stratum of soil, plants will grow in the surface soil, but their roots will not penetrate the lower layer at all. Should the soil contain much lime, large dressings of ferrous sulphate may be applied without injury, especially if this be done some time before crops are sown. A dressing at the extreme rate of 20 kilos. per square metre incorporated with a soil containing 19 per cent. of calcium carbonate was more of less injurious to peas and oats sown the same day; many of the plants failed, but those of the oats which grew were not inferior to those grown in plain soil. After removing the peas and oats, white mustard was sown on the same plots and flourished normally; at this

date no free acid or soluble iron salt could be detected in the soil at any depth. Determinations of total solids, ash, phosphoric acid, potash, and iron in the peas and oats grown with or without a heavy dressing of ferrous sulphate exhibited no differences which could be traced to the influence of this salt. The conclusions of Griffiths on this point are in contradiction with those of the authors.

To sum up, they consider ferrous sulphate beneficial only where the soil contains an excess of lime; its direct effect is to produce gypsum, to which much of the benefit must be ascribed, although there may be secondary benefits; the proportion of phosphoric acid in the crops raised with ferrous sulphate is not increased, nor is that of potash decreased, as was the case in Griffith's experiments.

J. M. H. M.

Analytical Chemistry.

Potassium Hydrogen Tartrate in Volumetric Analysis. By A. BORNTRAEGER (*Zeit. angew. Chem.*, 1892, 294).—The author, some time ago, proposed to use potassium hydrogen tartrate for the standardising of volumetric alkali. He now points out that the salt may be conveniently used to prepare normal alkali without the use of a normal acid. To prepare normal soda, an approximately prepared solution of sodium hydroxide, which must be free from carbonic acid, is added to a hot solution of 3.7626 gram of potassium hydrogen tartrate, until the liquid is neutral. If less than 20 c.c. of the alkali is required, the soda must be proportionally diluted.

L. DE K.

Gas-volumetric Estimation of Iodine. By L. MARCHLEWSKI (*Zeit. angew. Chem.*, 1892, 205—206).—The author, who at first did not get satisfactory results with Baumann's gas-volumetric method, has now, however, been very successful when following Baumann's latest directions (compare this vol. ii, 87).

L. DE K.

Estimation of Nitrogen by Kjeldahl's Method. By O. BÖTCHER (*Landw. Versuchs-Stat.*, 41, 170—173).—In estimating nitrogen in substances free from nitrates, Wilfarth's modification of Kjeldahl's method was found to be the most suitable. Copper sulphate was employed for a long time, until it was found that with substances which are difficult to decompose, such as horn meal, fish meal, &c., considerably more nitrogen was found when mercury was used than with copper sulphate, although the boiling with copper sulphate was continued as long as possible (4—5 hours), and the liquid was colourless when cold. With mercury, two hours' boiling is sufficient; and it was found unnecessary to add potassium sulphide and zinc before distilling, 1.5 gram of zinc dust being sufficient. In view of the many essential alterations made from time to time in the Kjeldahl method, Stutzer has proposed to substitute the name "sulphate method."

N. H. M.

Estimation of Nitric Nitrogen. By O. BÖTTCHER (*Landw. Versuchs-Stat.*, **41**, 165—169).—The following method was found to give very good results, both with Chili saltpetre and with the most various mixed manures:—The saltpetre (10 grams) is dissolved in water (500 c.c.), and of this solution, 25 c.c. put into a 400 c.c. distilling flask with water (about 120 c.c.), washed and dried zinc dust (5 grams), powdered iron (5 grams), and aqueous soda (80 c.c. of 32° R.). The flask is then connected with a condenser provided with a receiver, containing 20 c.c. of titrated sulphuric acid, and after one or two hours, 100 c.c. is distilled off, and titrated as usual. A number of analyses made by the method are given.

N. H. M.

Modified Gunning-Kjeldahl Method for use in presence of Nitrates. By A. L. WINTON (*Chem. News*, **66**, 227—228).—The following modification of the Gunning-Kjeldahl method is suggested to render it available in the presence of nitrates. 0.5 or 1 gram is digested for two hours, with 80 c.c. of a mixture containing 2 grams of salicylic acid for every 30 c.c. of sulphuric acid, the mixture being frequently agitated, 2 grams of zinc dust is then added, shaking continuously, and after heating the flask gently, until dense fumes cease to be evolved, 10 to 12 grams of potassium sulphate is added, the boiling being continued to complete oxidation. Water is carefully added to and shaken with the mixture, as the latter commences to solidify on cooling; the subsequent distillation with soda is conducted in the usual manner.

D. A. L.

Microchemical Localisation of Phosphorus in the Tissues. By L. LILIENFELD and A. MONTI (*Zeit. physiol. Chem.*, **17**, 410—424).—See this vol. ii, 135.

Gravimetric Estimation of Sulphuric Acid. By M. WEINIG (*Zeit. angew. Chem.*, 1892, 204—205).—The author recommends the following process:—An accurately measured quantity of the acid is introduced into a weighed platinum dish, and mixed with a very small excess of ammonia. The solution is evaporated to dryness, and the residue is finally dried for half-an-hour at 115—120°. After cooling in a desiccator, the whole is weighed. The sulphuric acid is then calculated from the amount of ammonium sulphate thus obtained. The results are said to be more accurate than those obtained by precipitation with barium chloride.

L. DE K.

The Action of Benzoic Chloride on Ammonia. By V. LEHMANN (*Zeit. physiol. Chem.*, **17**, 404—409).—Benzoic chloride is a reagent much used for the separation of diamines and other substances from urine.

When shaken with ammonia, benzamide is formed. The benzamide can be obtained by repeated shaking of the aqueous solution with ether. This may cause a small error in those analyses of urine in which benzoic chloride is used. The reagent does not act, however, on urea, or on creatinine.

W. D. H.

Estimation of Urea. By E. BÖDTKER (*Zeit. physiol. Chem.*, **17**, 140—147).—The best method of estimating urea is found to be that of Sjöqvist and Mörner (*Abstr.*, 1891, 146). W. D. H.

Volumetric Estimation of Alkaloids. By L. BARTHE (*Compt. rend.*, **115**, 512—514).—All the well-known vegetable alkaloids are alkaline to litmus, but are neutral to phenolphthaleïn. It follows that if a solution containing an alkaloid is titrated with sodium or potassium hydroxide, using litmus as an indicator, the alkali used will correspond with the quantity of free acid in the liquid, but if phenolphthaleïn is the indicator, the quantity of alkali used will correspond with the sum of the acid present in the free state and the acid present in combination with the alkaloid. The difference between the two titrations gives the quantity of acid in combination with the alkaloid.

The quantity of alkaloid taken should be about 0.001 of a gram-equivalent, and should be dissolved in 10 or 20 c.c. of decinormal acid and mixed with 20 c.c. of alcohol of 90°. For the titration with litmus the alcohol should be omitted.

The method is not applicable in the case of atropine or narcotine, but the results are not affected by the presence of salts of the alkalis or alkaline earths, or of salts of certain metals such as zinc.

It is obvious that in the case of crystallised salts, the method is applicable to the determination of water of crystallisation, since titration with litmus as indicator then gives the quantity of combined acid, and titration with phenolphthaleïn gives the quantity of alkaloid.

C. H. B.

Estimation of the Nitrogenous Constituents of Commercial Peptone. By A. STUTZER (*Zeit. anal. Chem.*, **31**, 501—515).—The value of commercial peptones depends essentially on the amount of albumose and peptone they contain. Gelatin and gelatin-peptone, leucine, tyrosine, and other decomposition products are comparatively valueless. The following process is directed to the estimation of these constituents:—In all cases, the amount of any precipitate is not found by weighing, but is calculated from the result of a nitrogen estimation by Kjeldahl's process, on the assumption that they all contain 16 per cent. Of dry preparations 5 grams is taken; of fluids, 20—25 grams. This is warmed with 200 c.c. of water, feebly acidified with acetic acid, boiled, and filtered, the filtrate being made up to 500 c.c. The filter, with the moist precipitate, is at once submitted to Kjeldahl's process, and a correction is made for the nitrogen in the paper. This gives the amount of unchanged albuminous substances. In a well made preparation these should not be present. The nitrogen in the filtrate is also determined, and the sum of the two stated as total nitrogen. A fresh portion of substance, dissolved in 25 c.c. of water (or, if a liquid, 50 c.c. concentrated to 25 c.c.), is gradually mixed with 250 c.c. of absolute alcohol, and filtered after 12 hours. The filtrate, which contains the gelatin-peptone, the leucine, tyrosine, and other decomposition products, is freed from alcohol and dissolved in water. Any insoluble matter is filtered off, and regarded as albumose. The clear solution is made up to 500 c.c., and 100 c.c. of this, warmed

to about 40° , is precipitated with 10—15 c.c. of a paste of mercuric oxide, containing about 15 per cent., and prepared by pouring mercuric chloride into dilute soda, washing thoroughly, and preserving in the dark. After stirring for a few minutes, the mixture is filtered and the nitrogen determined in the precipitate and filtrate. The former contains the gelatin-peptone, with unknown decomposition products of albumose and peptone. The filtrate contains the leucine, tyrosine, and other products of a digestive fermentation which has been carried to excess, together with part of the so-called flesh bases (creatine, &c.), which are very sparingly soluble in 95 per cent. alcohol. Instead of mercuric oxide, phosphotungstic acid may be used. This reagent, used in excess, precipitates none of the flesh bases except xanthine and hypoxanthine, of which, from their sparing solubility, only traces can be present in the alcoholic solution.

The alcohol precipitate containing the albumose, gelatin, and peptone is rinsed with water into a beaker and warmed until the alcohol is expelled. Any albumose which has been rendered insoluble is filtered off and washed with hot water. The clear solution is made up to 500 c.c., and of this, 50 c.c., mixed cold with an equal volume of dilute sulphuric acid (1 vol. to 3 vols. of water), is completely precipitated with phosphotungstic acid. The nitrogen in the precipitate gives the joint amount of the albumose, peptone, and gelatin. 100 c.c. of the same solution, concentrated on the water-bath to 8—10 c.c., is mixed with 100 c.c. of a cold saturated solution of ammonium sulphate. The precipitate is collected and washed with a saturated solution of ammonium sulphate. It is then dissolved in tepid water, and whilst one portion of the solution is used for nitrogen estimation, another is precipitated by barium chloride, to ascertain the amount of adhering ammonium sulphate. (The relation of the ammonia to the sulphuric acid in the solution used should be determined, not calculated.) The corrected nitrogen in the precipitate gives the amount of albumose and gelatin. The peptone is known by difference, its actual presence being confirmed by concentrating the remainder of the solution, precipitating the albumose and gelatin by solid ammonium sulphate, and testing the filtrate by adding a trace of cupric sulphate and a large excess of strong soda solution. Peptone gives a characteristic red colour.

The gelatin is best estimated by means of the viscosimeter, the viscosity being compared with that of a standard solution of the best white gelatin, to which an equal volume of a 20 per cent. solution of serum peptone, free from gelatin, has been added. A 10 per cent. solution of the substance is prepared and cooled for three hours to a temperature lower than that at which the comparison is to be made. It is then gradually warmed to a standard temperature, and immediately examined for viscosity. Very dilute solutions may be compared at $0-1^{\circ}$, whilst strong ones may need to be warmed to 25° , but it is not permissible to warm above the standard temperature, and again cool just before testing. Calling the viscosity of a 10 per cent. solution of serum peptone 100, the addition of 0.25 per cent. of gelatin raises it to 130 at $0-1^{\circ}$, 114 at 15° , 106 at 20° .

Having now ascertained the amount of nitrogen in the alcohol

precipitate in the form of albumose, peptone, and gelatin, the remaining nitrogen is to be regarded as belonging to the flesh bases. The principal of these is creatine, with 32·8 per cent. of nitrogen, whence the multiplication of the nitrogen by the factor 3·12, gives the total amount of the bases with but small error.

M. J. S.

Detection of Resin in the Sizing of Paper. By W. HERZBERG (*Chem. Centr.*, 1892, ii, 275; from *Mitt. k. tech. Vers.-Anstalt, Berlin*, 10, 80—85).—A piece of the paper to be examined is placed on a support and over a hole in the latter, so that the paper can be seen by transmitted light; 4—6 drops of ether are then allowed to fall on it.

If the paper has been sized with resin, a bright, translucent ring of resin is left after the ether has evaporated; if a mixture of resin with gelatin has been used, a repetition of the treatment may be necessary in order to obtain the ring. Paper sized with gelatin only leaves no such ring.

C. F. B.

Analysis of Sealing Wax. By C. MANGOLD (*Zeit. angew. Chem.*, 1892, 75—76).—Five grams of the powdered sample is boiled in a 250 c.c. flask with 150 c.c. of alcohol on a water-bath. After cooling, alcohol is added to the mark, and after thorough mixing and settling, 50 c.c. is pipetted off and mixed with an excess of Hübl's reagent. The portion insoluble in alcohol is filtered through a tared filter, dried at 110°, and weighed. It generally consists of chalk or magnesia, plaster of Paris, zinc-white, barytes, or even china clay, or tripoli. The colouring is, in the best brands, vermilion; in the inferior red ones, it generally consists of red oxide of iron, or red lead, whilst the black samples are mostly coloured with bone-black.

It is assumed by the author that the turpentine used in the manufacture of sealing wax has changed into colophony. Disregarding the mineral matter, sealing wax may, therefore, be taken to be a mixture of colophony and shellac. As there is an enormous difference between the iodine absorptions of colophony (115) and shellac (6), the iodine number of the sample affords ready means for the calculation of their respective percentages.

L. DE K.

Testing Linseed Oil Varnish. By W. FAHRION (*Zeit. angew. Chem.*, 1892, 171—173).—The author has found that linseed oil, on boiling and subsequent exposure, rapidly loses its power of absorbing iodine from Hübl's solution. The iodine numbers of three samples of boiled linseed oil, derived from the same original raw oil, had decreased respectively to 101·3, 77·3, and 73·7. The same effect is noticed on warming cotton-seed oil, which, instead of absorbing 108 per cent. of iodine, will then only take up about 70 per cent. The decrease in iodine absorbing power is, according to the author, not so much due to oxidation as to polymerisation.

With this decrease there is, however, a large increase in the amount of oxy-acids, which should, therefore, be estimated in every sample supposed to be stale (compare this vol., ii, 56).

L. DE K.

General and Physical Chemistry.

Absorption Spectra of Copper Salts in Aqueous Solution. By T. EWAN (*Phil. Mag.* [5], 33, 317—342).—The author has examined the absorption spectra of solutions of copper nitrate, chloride, and sulphate, employing Vierordt's method and a universal spectrophotometer by Krüss. The following is a summary of the results arrived at:—

1. The absorption spectra of the three salts examined undergo changes on diluting their solutions.

2. These changes are of such a nature that the spectra tend to become identical in dilute solutions.

3. The behaviour of the salts examined leads to the conclusion that, in strong solutions, the acid and basic parts of the salts are associated in producing absorption of light, whilst, in dilute solutions, they act independently in doing so.

4. These results are in substantial agreement with the hypothesis of electrolytic dissociation.

5. The results cannot be satisfactorily explained on the hypothesis of a hydrolytic dissociation, or on that of molecular aggregates.

J. W.

Difference of Potential at the Contact of mutually reacting Liquids. By J. BROWN (*Phil. Mag.* [5], 33, 532—539).—By a modification of Exner and Tuma's method, in which a water-dropping funnel and two filter-paper cylinders, saturated with the solutions under investigation and connected by a strip of filter paper, were used, the author has determined the difference of potential between the solutions, which were so chosen as to act on each other chemically. A reducing agent becomes positively electrified with respect to an oxidising substance with which it reacts, the difference of potential being, however, very slight. With respect to solutions which enter into double decomposition, there is no clear connection apparent between the observed electromotive forces and the heat equivalents of the reactions, but the concentration of the solutions has an effect.

There is a rough agreement between the heat of dilution of an aqueous solution (or the heat of solution of a pure liquid) and the difference of potential between it and water. The author finds that the rule that "water must show against every electrolytic solution the potential of the faster ion" does not hold good.

J. W.

Electromotive Forces of Gold and of Platinum Cells. By E. F. HERROUN (*Phil. Mag.* [5], 33, 516—520).—A cell was set up consisting of an amalgamated zinc rod immersed in a solution having the composition $\text{ZnCl}_2 + 400\text{H}_2\text{O}$, and of a platinum plate immersed in a solution of sodium platinochloride of the strength $\text{Na}_2\text{PtCl}_6 + 400\text{H}_2\text{O}$. The electromotive force of this cell between 12° and 15°

was, when first set up, about 1.7 volts, but afterwards it fell to an average value of 1.525 volts. The value calculated from thermochemical data is 1.548 volts.

A similar cell in which gold and auric chloride take the place of platinum and sodium platinochloride gave a mean electromotive force of 1.844 volts, or 0.2 volt below the calculated value. When a platinum plate was substituted for the gold plate and immersed in the solution of auric chloride, the electromotive force of the cell thus formed was found to be 1.782 volts, that is, less than the gold | auric chloride, but greater than the platinum | platinic chloride combination. Gold has the slightly higher potential when it is immersed along with a plate of platinum in pure water, or in dilute hydrochloric acid. In strong hydrochloric acid, the difference of potential is doubtful, and in nitro-hydrochloric acid, the platinum has the higher potential.

J. W.

Electromotive Force of Galvanic Combinations. By W. HITTORF (*Zeit. physikal. Chem.*, **10**, 593—620).—Ammonium nitride, NH_4N_3 , is decomposed in aqueous solution by the electric current with evolution of nitrogen at the anode and hydrogen at the cathode in the proportion of three volumes to one. Although the compound decomposes into its elements with considerable development of heat, it requires an electromotive force of more than a volt to effect the electrolytic decomposition.

The author studies various liquid elements with regard to their forces and the relation between these and the thermochemical data of the reactions taking place in the elements.

J. W.

Chemistry of the Secondary Battery. By M. CANTOR (*Ann. Phys. Chem.* [2], **47**, 424—425).—The author defends his former view that no hydrogen is occluded by the lead cathode in a secondary cell (compare Abstr., 1891, 514) against criticisms offered by Neumann and Streintz (*Ann. Phys. Chem.* [2], **46**, 431).

J. W.

Chemical Equilibrium in Mixed Electrolytes. By G. GORE (*Phil. Mag.* [5], **33**, 342—351).—By his voltaic method (compare Abstr., 1892, 930), the author has examined the equilibrium in various mixed electrolytic solutions, and sums up his results as follows:—The mixtures examined were divisible into two classes, namely, those which spontaneously changed with such rapidity that, on mixing, they at once attained a comparatively fixed state of chemical equilibrium, and those which only slowly changed and attained such a state. With mixtures of acids + salts, and of salts + salts, a fixed state of equilibrium was in nearly all cases immediately attained; but with halogens + salts, halogens + acids, and halogens + bases, a greater or less degree of retardation was frequently observed. Doubling the degree of concentration of the solution did not produce any conspicuous effect on the state of equilibrium. Twenty-four hours elapsed before halogens reached a state of comparative equilibrium with the potassium haloids in solution. The influence of rise of temperature in promoting a rapid attainment of

the final state is very great. When the ingredients of a mixture of halogen and salt (or acid) in water were in equivalent proportions, complete change was accelerated; if the salt or acid was in excess, it was retarded, and excess of halogen had no effect. The addition of caustic alkali to a solution of a halogen considerably retarded the rate of change which occurred on heating, the greatest retardation occurring with chlorine and the least with iodine. J. W.

Conductivity of Electrolytes in various Solvents. By I KABLUKOFF (*J. Russ. Chem. Soc.*, **23**, 391—422).—A solution of hydrogen chloride in various solvents gave the following resistances in ohms:— v is the dilution, that is, the volume in litres in which 1 gram molecule of the acid was dissolved.

Solvent.	v .	Resistance.
Benzene	4.34	12×10^6
Xylene	2.5	72×10^6
Hexane	12.5	48×10^6
Ethyl ether	2.5	14×10^6

The molecular conductivity (μ) of the same substance was found at 25° to be as follows:—

Solvent.	v .	μ .
Water	∞	394.00
Methyl alcohol	97.16	117.06
Ethyl alcohol	100.0	27.16
Propyl alcohol	35.47	9.74
Isobutyl and ethyl alcohols	49.3	10.46
Isobutyl alcohol.....	136.3	4.00
Isoamyl alcohol	25.42	1.25
Ether	3.52	0.000039

For acids dissolved in mixtures of alcohol and water, the following relative numbers for the conductivity were obtained, the conductivity of hydrochloric acid being taken as 100:—

$$v = 4$$

Alcohol per cent.	HCl.	H ₂ SO ₄ .	CCl ₃ -COOH.	CH ₂ Cl-COOH.
10	100	59.64	79.40	8.80
20	"	61.51	75.70	6.18
30	"	59.70	68.79	5.02
40	"	52.38	—	4.47
50	"	47.66	—	2.87
60	"	ca. 53.77	44.00	2.70
70	"	61.50	—	1.91
80	"	53.80	—	1.21

$$v = 8.$$

Alcohol per cent.	HCl.	H ₂ SO ₄ .	CCl ₃ -COOH.	CH ₂ Cl-COOH.
10	100	59.23	82.99	10.07
30	"	62.43	79.75	7.08
40	"	53.55	70.20	6.12
50	"	46.61	55.21	3.82
60	"	55.00	55.30	3.68
80	"	57.28	37.74	1.68

J. W.

Electrolytic Conductivity of Stereoisomeric Acids. By N. ZELINSKY (*J. Russ. Chem. Soc.*, **23**, 612—632).—The author has examined solutions of various isomeric acids with respect to their electrolytic conductivity, using Ostwald's method. He considered it probable that solutions of stereoisomeric acids, mixed in equal proportions, would give a dissociation constant equal to the mean of the constants of the acids separately, but that structurally isomeric acids would give a value different from the mean. The results of his experiments do not bear out this view, many exceptions occurring.

J. W.

Note by Abstractor.—The author is evidently unacquainted with the theory of isohydric solutions of Arrhenius, according to which equimolecular solutions of any acids would, when mixed, give a dissociation constant nearly equal to the mean of the separate constants, provided that these did not differ greatly from each other. If they did differ to any great extent, then the constant of the mixed solution would fall away considerably from the mean, and would not remain constant for different dilutions. These deductions are amply confirmed by the data obtained by the author. Isomerism does not affect the question directly at all.

Laws of the Expansion of Liquids compared with those relating to Gases and the Form of the Isothermals for Liquids and Gases. By E. H. AMAGAT (*Compt. rend.*, **115**, 919—923).—The coefficient of expansion of liquids by heat diminishes regularly as the pressure increases. It also increases regularly with the temperature; the increase da/dt diminishing as the pressure increases; so that, with ether under a pressure of 1000 atmospheres, the increase is practically nothing, although with alcohol under the same pressure it is still observable. The general form of the isothermals for liquids, taking p as abscissæ and pv as ordinates, is similar to that of the isothermals for gases.

H. C.

Relation between Heats of Formation and Temperatures of Reaction. By M. PRUD'HOMME (*Compt. rend.*, **115**, 1307—1308).—Sulphuric acid combines with potassium hydroxide, sodium hydroxide, and ammonia at the *absolute temperatures* 183°, 193°, and 213° respectively; it acts on metallic potassium at 205° and on sodium at 223°. Nitric acid acts on the alkalis at somewhat lower temperatures than sulphuric acid. Now the heats of formation of the solid salts from the hydrated acid and solid hydrated bases are

$\frac{1}{2}\text{K}_2\text{SO}_4$	40.7 Cal.	KNO_3	42.6 Cal.
$\frac{1}{2}\text{Na}_2\text{SO}_4$	34.7 „	NaNO_3 ..	36.1 „
—	—	NH_4NO_3 ..	34.0 „

It follows that the temperatures of reaction are lower the higher the heats of formation of the product, and this agrees with the law already enunciated by Berthelot.

For the same series of compounds, the product of the heat of formation Q into the *absolute* temperature of reaction T is practically constant. In the case of potassium, sodium, and ammonium sulphates, the numbers are 626, 629, and 601 respectively, and for sodium and potassium nitrates 216 and 213 respectively.

It is well known that in the same series of salts the molecular specific heat $M \times C$ is practically constant, and hence

$$Q \times T = K \times M \times C \text{ or } \frac{Q}{M} = K \frac{C}{T}.$$

For the same series of compounds, the heat of formation of the unit of mass is proportional to the specific heat and inversely proportional to the absolute temperature at the point of reaction.

C. H. B.

Thermochemistry of Isomeric Allyl and Propenyl Derivatives. By F. STOHMANN and H. LANGBEIN (*J. pr. Chem.* [2], 46, 530—546; compare Abstr., 1890, 100; 1891, 11; 1892, 763).—Eykmann (Abstr., 1890, 748) has demonstrated the ease with which the labile allyl derivatives, such as safrole, methyleugenol, &c., may be converted into the stable isomeric propenyl derivatives. The thermochemistry of these was ascertained by combustion in oxygen at 25 atmospheres pressure in a Berthelot's bomb, as already described. The results are given in the following table (p. 154).

It will be noted in each case the change of the labile allyl derivative into the stable propenyl derivative is accompanied by a loss of energy, the heat of combustion of the propenyl derivative being from 8.8 to 11.1 Calories lower than that of the allyl derivative; this is in accord with the other cases which have been studied (compare Abstr., 1890, 100; 1892, 763). Compounds like eugenol and betelphenol, which differ only in orientation, have practically the same heat of combustion. Attention is called to the higher specific gravity refractive index, and melting point of the propenyl derivatives as compared with the allyl derivatives. The \pm energy change which accompanies various reactions, such as substitution of OH for H (Abstr., 1892, 763), $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ for H, and $\text{CH}\cdot\text{CH}\cdot\text{CH}_3$ for H, are compared with the cases which have been already published. These results, and others shortly to be detailed, confirm the authors in their belief that the opening up of the ethylenic linking by the addition of two hydrogen atoms is not accompanied by a constant accession of energy, as would be deduced from Horstmann's figures (*Ber.*, 21, 2217).

	Mol. weight.	Heat of combustion at constant pressure per gram molecule, Cal.	Heat of formation, Cal.	Aggregation.
<i>Allyl derivatives—</i>				
Methylchavicol, $C_{10}H_{12}O$	148	1335·1	18·9	liquid.
Eugenol, $C_{10}H_{12}O_2$	164	1286·9	67·1	„
Eugenol acetate, $C_{12}H_{14}O_3$	206	1498·5	112·5	solid.
Eugenol benzoate, $C_{17}H_{16}O_3$...	268	2065·3	84·7	„
Betelphenol, $C_{10}H_{12}O_2$	164	1286·9	67·1	liquid.
Betelphenol benzoate, $C_{17}H_{16}O_3$	268	2065·4	84·6	solid.
Methyleugenol, $C_{11}H_{14}O_2$	178	1459·4	57·9	liquid.
Safrole, $C_{10}H_{10}O_2$	162	1244·7	40·3	„
Apiole, $C_{12}H_{14}O_4$	222	1499·6	111·4	solid.
<i>Propyl derivatives—</i>				
Anethoil, $C_{10}H_{12}O$	148	1324·2	29·8	solid.
Isoeugenol, $C_{10}H_{12}O_2$	164	1278·1	75·9	liquid.
Isoeugenol acetate, $C_{12}H_{14}O_3$..	206	1489·0	122·0	solid.
Isoeugenol benzoate, $C_{17}H_{16}O_3$..	268	2056·1	93·9	„
Methylisoeugenol, $C_{11}H_{14}O_2$	178	1448·0	69·0	liquid.
Ethylisoeugenol, $C_{12}H_{16}O_2$	192	1602·9	77·1	solid.
Isosafrole, $C_{10}H_{10}O_2$	162	1234·5	50·5	liquid.
Asarone, $C_{12}H_{16}O_3$	208	1576·8	103·2	solid.
Isosapiol, $C_{12}H_{14}O_4$	222	1489·0	122·0	„
Anisoil, C_7H_8O	108	905·5	28·5	liquid.

A. G. B.

Estimation of the Vapour Density of Iodine in different Atmospheres. By E. THIELE (*Zeits. anorg. Chem.*, **1**, 277—284).—The author's experiments were made to ascertain the influence of foreign molecules on the vapour density of iodine. Preliminary experiments in an ordinary V. Meyer's apparatus in atmospheres of nitrogen, oxygen, and hydrogen chloride showed that the presence of these gases is without influence. Further experiments were then made in a modification of this apparatus, which is described with the aid of a drawing. In the presence of ether vapour, and at the temperature of boiling sulphur, iodine gives much lower values for the vapour density than the normal ones; but it was subsequently found that iodine acts on ether at this temperature, so that it is doubtful if the low values are due to dissociation. In the presence of chloroform vapour, a normal value was obtained.

A. R. L.

Vapour Pressure of Aqueous Alcoholic Solutions of Salts. By I. KABLUKOFF (*J. Russ. Chem. Soc.*, **23**, 388—391).—The author finds that when sodium chloride is dissolved in a mixture of water and ethyl alcohol, the vapour pressure of the solvent, instead of being lowered, as is the case with a pure liquid, is increased. The following numbers were obtained by him for a mixture of alcohol and water of sp. gr. 0·973 at 20°:—

t° .	h .	h' .	$\frac{h-h'}{h}$.	v .
19.5	24.79	25.99	-0.048	1.0
18.5	20.87	24.31	-0.165	0.5

In the table, h denotes the vapour pressure of the solvent, h' that of the solution, and v the number of litres in which 1 gram molecule of the salt is dissolved. J. W.

Density of Sulphuric acid Solutions. By S. U. PICKERING (*Phil. Mag.* [5], 33, 463—466). In answer to Rücker's further remarks on this subject (see this vol., ii, 61), the author points out that he did not offer a fresh solution (with one break) of his results, but simply showed that one of the four breaks first mentioned, namely, that which he had always considered to be very feebly marked, could be bridged over by the use of a more complicated parabola, but that there were reasons against the acceptance of this simplification. In the author's opinion, the "no break" curve contributed by Rücker is "an artificial and highly improbable representation of physical facts," whereas his own "four break" representation is not only very probable, but is unique inasmuch as it affords an interpretation in harmony with all the other properties studied. The concordance of these various results, he contends, is, indeed, the chief argument in favour of his views. S. U. P.

Some Experiments on the Diffusion of Substances in Solution. By S. U. PICKERING (*Phil. Mag.* [5], 35, 127—134).—Weak solutions of electrolytes were allowed to diffuse from open jars into very large volumes of water. The rate of diffusion being proportional to the translational velocity of the molecules, the relative values of mv^2 were thus obtained, and these were compared with the osmotic pressures of the solutions as determined from their freezing points. If osmotic pressure is due to the impact of free dissolved or quasi-gaseous molecules, the molecular weights which give the osmotic pressures as constant ought also to give mv^2 as a constant when determined from the rate of diffusion. But this was not found to be the case; the values were 16 times greater in some instances than they were in others. Substances with large molecular weights gave the largest values for mv^2 . S. U. P.

Relations of the Physical and Chemical Properties of the Chemical Elements and Compounds. By H. FRITZ (*Monatsh.*, 13, 743—834).—The author has collected data with respect to the cohesion of elements and compounds, and shows that certain relationships hold good between the force of cohesion and other physical and chemical properties. The results have been for the most part already published in other papers. H. C.

Influence of Electrolytic Dissociation on the Decomposition of Ammonium Nitrite in Aqueous Solution. By A. ANGELI and G. BOERIS (*Gazzetta*, 22, ii, 349—351).—The fact that concentrated aqueous solutions of ammonium nitrite are much more readily de-

composed by heat than when dilute suggests that this is caused by the electrolytic dissociation in the case of the former being less far advanced than in more dilute solutions. If this be so, the addition to the solution of salts having one ion in common with ammonium nitrite should produce the same effect as an augmentation of concentration. This is found to be the case; the speed of decomposition by heat of dilute ammonium nitrite solutions is greatly increased by the addition of ammonium chloride, ammonium sulphate, potassium nitrite, or sodium nitrite, whilst the addition of sodium chloride, sodium acetate, or magnesium sulphate does not alter the rate of decomposition. The authors are continuing the investigation.

W. J. P.

Cryoscopy, &c., of Ammoniometallic Compounds. By J. PETERSEN (*Zeit. physikal. Chem.*, **10**, 580—592).—The molecular weights of ammoniacal platinum, cobalt, and chromium compounds, as determined from the freezing points of their aqueous solutions, with the help of Raoult's empirical constants, give results agreeing very well with the formulæ usually assumed to be correct. The most marked exceptions are formed by the rhodo- and erythro-salts, which, however, in all probability decompose in solution.

The electrical conductivity of solutions of the same salts was also determined at 18°, and the author presents his results in tabular and curve form. The values of i obtained by the two methods show in general a good agreement.

J. W.

Behaviour of Indole and some of its Derivatives with respect to Raoult's Law. By A. FERRATINI and F. GARELLI (*Gazzetta*, **22**, ii, 245—269).—The high results obtained in molecular weight determinations by the cryoscopic method when naphthalene is used as a solvent, for substances such as indole, β -methylindole, $\alpha\beta$ -dimethylindole, carbazole, indene, and α -naphthol have led the authors to investigate the cause.

The molecular depressions of the freezing point of other solvents by these substances are quite normal; the formation of solid solutions on freezing seemed therefore probable (compare Van Bijlert, *Abstr.*, 1891, 1411). By means of a specially constructed apparatus, the crystals deposited on cooling a solution of indole in naphthalene were separated from the solution, then washed with ether, and analysed. Control experiments were also made with solutions of α -methylindole, which gives normal results with naphthalene as a solvent; this was done in order to determine what proportion of the dissolved substance was taken up by the separating crystals as a mere mechanical inclusion. The amount of indole found in the solidified naphthalene was far greater than that of the α -methylindole; the proportion of the latter gives an approximate measure of the quantity of indole carried down mechanically by the naphthalene. The excess of indole found in the naphthalene should, therefore, be present in a state of solid solution, 38—40 per cent. of the indole dissolved crystallises with the naphthalene, and of this only one-half is carried down mechanically. The above explanation is rendered much more

probable by the fact that those substances which give high molecular weights are very similar in constitution to the solvents employed.

Quite another hypothesis must be devised to explain the small depression of the freezing point of naphthalene caused by benzoic acid. The crystals separating on cooling the solution contain only some 3—4 per cent. of the acid present, merely as a mechanical inclusion. Beckmann (Abstr., 1891, 389) found that benzoic acid gives a high molecular weight by the boiling point method in benzene or chloroform solution, but normal values are obtained when acetic acid is used as the solvent; hence it is probable that the benzoic acid is present in such solutions as aggregates of high molecular weight.

W. J. P.

Stereochemistry of Nitrogen. By A. CLAUS (*J. pr. Chem.* [2], 46, 546—559).—This is a critique of the paper of Hantzsch and Miolati, on “Dissociation Constants of Stereoisomeric Nitrogen Compounds” (Abstr., 1892, 1268). Claus will not admit the necessity for stereoisomeric theories in this connection, position isomerism and kind of linking appearing to furnish sufficient explanation.

A. G. B.

Avidity of Acids in Aqueo-alcoholic Solutions. By I. KABLUKOFF (*J. Russ. Chem. Soc.*, 23, 459—487).—From an examination of the electrolytic conductivity of hydrogen sulphate, hydrogen chloride, lithium sulphate, and lithium chloride dissolved singly and together in various mixtures of alcohol and water, the author finds that the “avidity” of hydrogen sulphate with respect to hydrogen chloride is less in solutions containing alcohol than it is in pure water.

J. W.

Affinity of Organic Acids. By P. WALDEN (*Zeit. physikal. Chem.*, 10, 563—579, and 638—664; compare Abstr., 1892, 266).—The dissociation constants of the following tribasic acids were measured:—

	K.
Tricarballic acid, m. p. 158°	0·022
Unsymmetrical methyltricarballic acid, m. p. 180°	0·032
Unsymmetrical ethyltricarballic acid, m. p. 147—148°	0·032
Unsymmetrical propyltricarballic acid, m. p. 136°	0·031
Unsymmetrical isopropyltricarballic acid, m. p. 161°	0·043
p-Tetramethyltricarballic acid (?), m. p. 156°	0·0098
a-Tetramethyltricarballic acid (?), m. p. 133°	0·0111
Citric acid, m. p. 152—154°	0·082
βγ-Dicarboxy-γ-valerolactone, m. p. 168° (decomp.)	0·66
Aconitic acid, m. p. 180—183°	0·136
Ethenyltricarboxylic acid, m. p. 150°	0·32
Propenyltricarboxylic acid, m. p. 146°	3·305
Butenyltricarboxylic acid, m. p. 136—137·5°	0·307
Isobutenyltricarboxylic acid, m. p. 148°	0·334
αβ-Dimethylethenyltricarboxylic acid, m. p. 156—158°	0·503
Benzylethenyltricarboxylic acid, m. p. 168·5°	3·2

	<i>K.</i>
Ethylmethylcarboxyglutaric acid, m. p. 166°	0·974
Propylmethylcarboxyglutaric acid, m. p. 167°	1·02
Benzylmethylcarboxyglutaric acid, m. p. 178°..about	1·5
Unsymmetrical trimethylenetricarboxylic acid	0·91
Normal butanetetracarboxylic acid, m. p. 233°	0·040

The constants of a considerable number of aromatic derivatives of fatty acids were determined ; those of acetic acid derivatives are given below :—

	<i>K.</i>
Anilidoacetic acid, m. p. 127—128°	0·0038
Acetanilidoacetic acid, m. p. 194—195°	0·0260
Chloracetanilidoacetic acid, m. p. 130°	0·0340
Bromacetanilidoacetic acid, m. p. 152°	0·0340
Acetobromanilidoacetic acid, m. p. 176—177°	0·0285
Orthotoluidoacetic acid, m. p. 148—149°	0·00587
Acetorthotoluidoacetic acid, m. p. 210—212°	0·0219
Paratolylglycine (Bischoff, Hausdörfer), m. p. 112—114°	0·0015
Acetylparatolylglycine, m. p. 175—176°	0·0219
α -Naphthylglycine, m. p. 199°	0·004
Aceto- α -naphthylglycine, m. p. 156°	0·0207
β -Naphthylglycine, m. p. 133—136°	0·006
Aceto- β -naphthylglycine, m. p. 172°	0·0241
Phenylimidodiacetic acid, m. p. 150—155°	0·273
Orthotolylimidodiacetic acid, m. p. 158—162°	0·209
α -Naphthylimidodiacetic acid, m. p. 133—134°	0·051
β -Naphthylimidodiacetic acid, m. p. 182—183°	0·246

Other acids investigated were :—

	<i>K.</i>
Ethylmethylacetic acid, b. p. 175°	0·00170
Diethylacetic acid, b. p. 190°	0·00203
Iodacetic acid, m. p. 82°	0·075
α -Bromopropionic acid, m. p. 15—20°	0·108
β -Bromopropionic acid, m. p. 62·5°	0·0098
$\alpha\alpha$ -Dibromopropionic acid, m. p. 61°	3·3
$\alpha\beta$ -Dibromopropionic acid, m. p. 64°	0·67
α -Nitrosopropionic acid, m. p. 176—178°	0·050
β -Nitropropionic acid, m. p. 65—67°	0·0162
α -Bromobutyric acid	0·106

J. W.

Influence of the Constitution of the Alcohols on the Velocity of Etherification. By N. MENSCHUTKIN (*J. Russ. Chem. Soc.*, 23, 263—283).—The author gives the following table of the velocity constants of etherification for alcohols mixed in molecular proportion with acetic anhydride, diluted with 15 volumes of benzene, and heated at 100° :—

Primary Saturated Alcohols.

	Etherification constant.	Ratio to the constant of methyl alcohol.
$\text{CH}_3\cdot\text{OH}$	0.1118	100.0
$\text{CH}_3\cdot\text{CH}_2\cdot\text{OH}$	0.0542	48.4
$\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$	0.0480	42.9
$\text{CH}_3\cdot[\text{CH}_2]_2\cdot\text{CH}_2\cdot\text{OH}$	0.0465	41.6
$\text{CHMe}_2\cdot\text{CH}_2\cdot\text{OH}$	0.0401	35.9
$\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{CH}_2\cdot\text{OH}$	0.0393	35.1
$\text{CH}_3\cdot[\text{CH}_2]_6\cdot\text{CH}_2\cdot\text{OH}$	0.0377	33.7
$\text{CH}_3\cdot[\text{CH}_2]_{12}\cdot\text{CH}_2\cdot\text{OH}$	0.0291	26.0
$\text{CH}_3\cdot[\text{CH}_2]_{14}\cdot\text{CH}_2\cdot\text{OH}$	0.0269	24.0
$\text{CH}_3\cdot[\text{CH}_2]_{16}\cdot\text{CH}_2\cdot\text{OH}$	0.0245	21.9
$\text{CH}_3\cdot[\text{CH}_2]_{26}\cdot\text{CH}_2\cdot\text{OH}$	0.0174	15.5

Primary Unsaturated Alcohols.

$\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$	0.0287	25.9
$\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{OH}$	0.0267	23.9
$\text{CH}\cdot\text{C}\cdot\text{CH}_2\cdot\text{OH}$	0.0200	17.9
$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{OH}$	0.0280	25.0

Secondary Saturated Alcohols.

$\text{CHMe}_2\cdot\text{OH}$	0.0148	13.2
$\text{CHMeEt}\cdot\text{OH}$	0.0123	11.0
$\text{C}_6\text{H}_{13}\cdot\text{CHMe}\cdot\text{OH}$	0.00916	8.1

Secondary Unsaturated Alcohols.

$\text{C}_3\text{H}_5\cdot\text{CHMe}\cdot\text{OH}$	0.00643	5.7
$\text{CH}(\text{C}_6\text{H}_5)_2\cdot\text{OH}$	0.00258	2.3
$\text{CH}(\text{CH}_2\text{Ph})_2\cdot\text{OH}$	0.00108	0.96

Tertiary Alcohol.

$\text{CMe}_3\cdot\text{OH}$	0.00091	0.8
------------------------------------	---------	-----

Chloro-alcohols.

$\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$	0.0113	10.1
$\text{CHCl}_2\cdot\text{CH}_2\cdot\text{OH}$	0.00262	2.3
$\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{OH}$...	0.00523	4.5
$\text{CH}(\text{CH}_2\text{Cl})_2\cdot\text{OH}$	0.000338	0.3

Cyano-alcohols.

$\text{CN}\cdot\text{CH}_2\cdot\text{OH}$	0.0461	41.2
$\text{CN}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$	0.00896	8.0
$\text{CN}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$	0.00305	2.7

Ether Alcohols.

$\text{OAc}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$	0.0133	11.9
$\text{COOEt}\cdot\text{CH}_2\cdot\text{OH}$	0.0263	23.5
$\text{COOEt}\cdot\text{CHMe}\cdot\text{OH}$	0.00568	5.0

From these numbers, it appears that as the carbon chain in the alcohol lengthens, the constant diminishes, and this also occurs when the alcohol becomes unsaturated. The primary alcohols have a greater constant than the secondary, and these again than the tertiary alcohols. With regard to the substituted alcohols, the author draws a comparison between the influence of the substituting groups on the constant of etherification, and on the dissociation constant of acids as studied by Ostwald. In general, a group which increases the dissociation constant diminishes the etherification constant. J. W.

Rate of Sugar Inversion in Aqueo-alcoholic Solutions. By I. KABLUKOFF and A. TSAKONI [ZACCONI] (*J. Russ. Chem. Soc.*, **23**, 546—559).—The author has obtained the following velocity constants for sugar inversion at 25° in mixtures of alcohol and water under the influence of the acids given in the table:—

Solvent.	HCl.	H ₂ SO ₄ .	CCl ₃ ·COOH.	CH ₂ Cl·COOH.
Water	21·30	11·68	15·98	1·08
10 per cent. alcohol ..	20·80	10·82	12·21	0·785
20 " " ..	20·11	9·65	11·30	0·632
30 " " ..	18·68	8·33 (?)	7·32	0·380
40 " " ..	17·61	8·19	6·79	0·250
50 " " ..	16·66	7·36	5·12	0·199

Taking the value for hydrochloric acid as 100 in each case, the "affinity" of the acids in the various mixtures appears as follows:—

Acid.	Water.	10 p. c. alcohol.	20 p. c. alcohol.	30 p. c. alcohol.	40 p. c. alcohol.	50 p. c. alcohol.
HCl.....	100·0	100·0	100·0	100·0	100·0	100·0
H ₂ SO ₄	54·8	52·2	48·0	45·1 (?)	46·5	44·2
CCl ₃ ·COOH...	75·0	58·7	56·2	39·2	38·6	32·0
CHCl ₂ ·COOH.	5·1	3·8	3·1	2·0	1·4	1·2

J. W.

Reaction between Nitrites and Salts of Hydroxylamine. By C. MONTEMARTINI (*Gazzetta*, **22**, ii, 304—325).—The author has studied the velocity of the reaction occurring between hydroxylamine hydrochloride and sodium nitrite in aqueous solution represented by the equation $\text{NH}_2\cdot\text{OH}, \text{HCl} + \text{NaNO}_2 = \text{N}_2\text{O} + \text{NaCl} + 2\text{H}_2\text{O}$.

The velocity is deduced from the general formula $k = \frac{1}{T} \left(\frac{1}{C} - \frac{1}{C_0} \right)$,

where k is a measure of the velocity, C_0 the quantity of hydroxylamine initially present in grams per 100 c.c. of the solution, and C the quantity of hydroxylamine present T minutes after the commencement of the reaction. Equivalent quantities of hydroxylamine hydrochloride and sodium nitrite were used.

If C_0 be greater than 0.036 at 16° , k increases considerably as T increases; at this concentration, $k = 0.226$ at 25° , and is nearly constant. When T becomes greater than 400, however, the products of the reaction make their presence evident by diminishing k . The addition of sodium chloride, one of the products of the reaction, has a considerable effect on the velocity. When the solution contains 24.3 per cent. of sodium chloride, k falls to 0.026 at 25° ; even when this large excess is present, however, k decreases in magnitude for the higher values of T . The velocity becomes much greater as the temperature rises.

The product $k\eta$, where η is the constant of internal friction of the solution, is not a constant for solutions containing varying amounts of sodium chloride, in addition to the reacting constituents. Kajander found that $k\eta$ was constant in a number of reactions between acids and insoluble carbonates; these, however, were all reactions of the first order, one of the active substances being a solid. The present reaction is one of the second order, both the substances being in the liquid state, and the product $k\eta^2$ is approximately constant if large quantities of sodium chloride (16—24 per cent.) or sulphate (8—14 per cent.) be considered.

Sodium sulphate diminishes the speed of reaction in a similar manner to sodium chloride; tabulated results are given of experiments in which varying quantities of sodium sulphate are present in the solution. The author enunciates the law that in a reaction of the n th order, $k\eta^n$ is a constant when the acting substances are present in molecular proportion.

If one of the reacting salts be present in excess, kn should be constant during variations of n , because $-\frac{dC}{dT} = knC^2$, n being the ratio of the number of molecules of the one salt to that of the other. This was not verified, however, when the proportion of sodium nitrite present was varied.

With hydroxylamine hydrochloride, the velocity of reaction is less than when the sulphate is used, and still less than with the nitrate. With lithium, sodium, and potassium nitrites, k decreases as the atomic weight of the metal increases, and k is greater for strontium nitrite than for that of barium.

W. J. P.

Isomorphism. Part VII. By J. W. RETGERS (*Zeit. physikal. Chem.*, 10, 529—557; compare Abstr., 1891, 146, and 1151; Abstr., 1892, 1048).—Potassium ferrate, K_2FeO_4 , may be preserved for days in solution without undergoing decomposition, and may be crystallised at a gentle heat in microscopic, black prisms or sharp pyramids. It forms mixed crystals with potassium sulphate, selenate, chromate, tungstate, and molybdate, and is, therefore, isomorphous with these salts. The colour of the mixed crystals varies from pink through dark red to dark brown in the case of chromate. No mixed crystals could be obtained with potassium tellurate.

Potassium tellurate when crystallised out of more or less concentrated solutions of caustic potash appears in two forms, namely, feebly birefringent crystals of $K_2TeO_4 + 5H_2O$, and highly birefringent

crystals probably containing 2 mols. H_2O . Most likely it is the latter form which crystallises from potash solution along with potassium osmate, $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$, yielding brown, feebly dichroic crystals.

Potassium ruthenate crystallises neither with potassium sulphate and selenate, nor with potassium tellurate and osmate.

The author gives the following corrected table of the crystallographic relations of the sulphates, selenates, &c., of the potassium group:—

Rhombic	{	$\text{K}_2\text{SO}_4, \text{Am}_2\text{SO}_4, \text{Rb}_2\text{SO}_4, \text{Cs}_2\text{SO}_4, \text{Ti}_2\text{SO}_4.$
		$\text{K}_2\text{SeO}_4, \text{Rb}_2\text{SeO}_4, \text{Cs}_2\text{SeO}_4, \text{Ti}_2\text{SeO}_4.$
		$\text{K}_2\text{CrO}_4, \text{Rb}_2\text{CrO}_4, \text{Cs}_2\text{CrO}_4.$
		$\text{K}_2\text{MnO}_4, \text{Rb}_2\text{MnO}_4, \text{Cs}_2\text{MnO}_4.$
		$\text{K}_2\text{WO}_4.$
Monoclinic	{	$\text{K}_2\text{MoO}_4.$
		$\text{K}_2\text{FeO}_4.$
		$\text{Am}_2\text{SeO}_4.$
	{	$\text{Am}_2\text{CrO}_4.$
		$\text{Am}_2\text{MoO}_4.$

Ti_2CrO_4 , probably rhombic.

The sulphotungstates and sulphomolybdates of potassium and ammonium do not form mixed crystals with potassium or ammonium sulphate.

The author considers the birefringency and pleochroism of the mixed crystals of ammonium chloride and ferric chloride to be due to the inclusion in the crystal of $\text{Fe}_2\text{Cl}_6 + 7\text{H}_2\text{O}$, which is itself birefringent and pleochroic. Roozeboom's assumption that a regular modification of the ferric chloride exists in the mixed crystal, and that the optical properties are occasioned entirely by internal tension, appears to him unnecessary.

J. W.

Aluminium Apparatus in the Laboratory. By G. BORNEMANN (*Ber.*, 25, 3637—3642).—The author describes the efficiency and appearance of air and water baths, rings, clamps, &c., made of aluminium which he has used in the laboratory for some time. In accordance with the physical and chemical properties of aluminium, he finds that it is preferable to use it in many cases instead of copper and iron.

E. C. R.

New Drying Oven. By M. KAEHLER (*Ber.*, 25, 3612—3614).—The speciality of the apparatus consists in an inverted and truncated four-sided pyramid of brass which is inserted in the floor of the oven; it is closed at the top and is surrounded by another pyramid open at the top. The oven is heated by a burner placed under the inner closed pyramid, and the products of combustion pass from the top of this pyramid through four tubes which run up inside the corners of the oven, and help to maintain the temperature of the oven. A current of heated air which enters the oven through the space between the outer and inner pyramids is also continually passing through the oven.

E. C. R.

Laboratory Apparatus for Distillation with Superheated Steam. By B. JAFFÉ (*Ber.*, 26, 123—125).—Although easy on the large scale, the use of superheated steam in the laboratory is troublesome. The author finds that equally good results may generally be obtained by the use of the hot products of combustion of a bunsen flame. A copper tube of about 3—4 mm. diameter passes through the tubulure of the retort, and is bent at right angles outside the retort. The bunsen flame is placed immediately before the slightly expanded opening of this tube, and the heated products of combustion are drawn into it by means of a water pump connected with the receiver or receivers. The inner end of the copper tube may pass into the liquid in the retort, but the author finds it generally better for it to end just at the surface of the liquid. The presence of carbonic anhydride, nitrogen, and excess of atmospheric air does not prove prejudicial. Distillations of glycerol, paraffin, stearic acid, &c., have been successfully carried out by this method. L. T. T.

Inorganic Chemistry.

The Molecular Weight and Refractive Power of Hydrogen Peroxide. By G. CARRARA (*Gazzetta*, 22, ii, 341—349).—From experiments on the freezing points of aqueous solutions of hydrogen peroxide, Tammann (*Abstr.*, 1890, 106) concluded that the latter substance has the molecular formula H_4O_4 . The molecular depressions of the freezing point observed by Tammann differed greatly amongst themselves, and the method by which he deduced the formula H_4O_4 is open to criticism. Using solutions of very different concentrations, the author found the molecular depression of the freezing point to correspond fairly well with the molecular formula H_2O_2 . Tammann's discordant results are possibly due to catalytic decomposition of the solutions, induced by the platinum stirrer used by him; the author employed one of glass.

Determinations of the specific refraction of aqueous solutions of hydrogen peroxide also point to the simple formula H_2O_2 . The specific dispersion in aqueous solution is less than that of water, $\left(\frac{\mu_{H_2O_2} - \mu_{H_2O}}{d}\right) = 0.00747$; considering the substance as a compound of water and oxygen, the atomic dispersion of the second oxygen atom is 0.0867.

The absorption spectrum of the blue ethereal solution of the compound of chromic anhydride and hydrogen peroxide shows a band between $\lambda = 6.265$ and $\lambda = 5.380$. W. J. P.

Critical Examination of the Fundamental Determinations of Stas on Potassium Chlorate. By G. HINRICHS (*Compt. rend.*, 115, 1074—1078).—The author points out that in Stas's determination of the oxygen contained in potassium chlorate, the value found is a function of the amount of chlorate taken, so that calculated for

30—35 grams of chlorate $O = 16$, and for 100 grams of chlorate $O = 15.98$. Precise deductions cannot, therefore, be made from these determinations.

H. C.

Phosphorus Iodosulphide. By L. OUVARD (*Compt. rend.*, 115, 1301—1303).—Dry hydrogen sulphide has no action on phosphorus iodide at the ordinary temperature, but phosphorus iodosulphide, P_2S_3I , can be obtained (1) by heating phosphorus tri-iodide in a current of hydrogen sulphide at 110 — 120° until hydrogen iodide is no longer evolved; (2) by dissolving phosphorus, iodine, and sulphur in the proper proportions in carbon bisulphide, evaporating, and heating at 120° in a current of an inert gas; (3) by dissolving iodine in the proper proportions in a solution of phosphorus sulphide in carbon bisulphide. The iodosulphide crystallises from carbon bisulphide in somewhat bulky, brilliant, highly refractive, golden-yellow prisms, which seem to belong to the triclinic system. It is stable in dry air, but slowly decomposes in contact with moist air with evolution of hydrogen sulphide; it dissolves readily in carbon bisulphide, but is only slightly soluble in benzene or chloroform, and still less soluble in ether or absolute alcohol. When heated in presence of air, it melts at about 106° to a viscous liquid which easily remains in superfusion, and at about 300° it burns with formation of phosphoric anhydride, sulphurous anhydride, and iodine; when heated to 300° in a vacuum, it splits up into iodine and phosphorus sulphide. Cold water has very little effect, but hot water decomposes it rapidly, and fuming nitric acid attacks it with explosive violence and production of light.

C. H. B.

Properties of Dry Hydrogen Sulphide. By R. E. HUGHES (*Phil. Mag.* [5], 33, 471—475).—Hydrogen sulphide, dried by passing over calcium chloride and phosphoric anhydride, has no action on magnesia, baryta, ferric oxide, or on salts of silver, copper, mercury, lead, bismuth, arsenic, cadmium, antimony, tin, or cobalt. It does not redden dry blue litmus paper.

J. W.

Action of Potassium Permanganate on Sodium Thiosulphate. By C. LUCKOW (*Zeit. anal. Chem.*, 32, 53—57).—A solution of sodium thiosulphate, whether neutral, acidified by sulphuric acid, or made alkaline with potash, when boiled with an excess of potassium permanganate, reduces only so much of the latter as corresponds with what is required by the equation $2H_2S_2O_3 + O_7 + H_2O = 2H_2SO_4 + H_2S_2O_6$, and it is stated that the dithionic acid can be detected in the oxidised solution.

M. J. S.

Volatilisation of Silica. By E. CRAMER (*Zeit. angew. Chem.* 1892, 484—486).—Although a sublimate of pure silica is occasionally observed in the upper region of blast-furnaces, no experiments on the small scale have been recorded to prove its volatility. The author has therefore made some experiments with pure crystallised native silica. A Deville oven, of 12 cm. diameter and 33 cm. in height, was heated by means of graphitic carbon, whilst a blast of air was forced through from below. After two hours, a heat was obtained equal to the highest ever noticed in furnaces; at this

platinum not only rapidly melted, but actually began to boil and to evaporate.

A weighed quantity of crystallised quartz was introduced in a graphitic crucible provided with a lid. This crucible was put inside a magnesite crucible, the empty space being filled up with finely powdered magnesia. The crucibles were now put into the furnace, a strong blast was applied, and, after 4 kilos. of graphite had been burnt, the experiment was stopped and the quartz reweighed, when it was found to have lost 40.5 per cent. in weight. By thrice repeating the fusion, the author succeeded in completely volatilising the quartz. Another experiment showed, that no volatilisation takes place in covered crucibles at the temperature of melting iron.

L. DE K.

Density of Carbonic Oxide, and the Atomic Weight of Carbon. By A. LEDUC (*Compt. rend.*, 115, 1072—1074).—The carbonic oxide was prepared by the action of sulphuric acid on oxalic acid, and was purified by means of potassium hydroxide, and dried over phosphoric anhydride. Three experiments made in the manner previously described gave, for the weight of the gas at 0° and 760 mm., (i) 2.8470; (ii) 2.8468; (iii) 2.8469 grams: the mean being 2.8469. The weight of air in the same vessel is 2.9440 grams, and hence the relative density of the carbonic oxide is 0.96702. This result agrees with the generally accepted value. Assuming that at 0° this gas has the same molecular volume as oxygen, the atomic weight of carbon, calculated from this determination, is 11.913 ($O = 15.88$), which agrees very closely with the numbers 11.915 and 11.917, obtained by synthesis by Van der Plaats and Friedel respectively. If the experimental results are taken as correct, the ratio of the molecular volume of carbonic oxide to that of oxygen is 1.0001. It has been shown that the corresponding ratio for hydrogen and oxygen is about 1.002.

If Regnault's value for oxygen (1.10563) is assumed to be true, the atomic weight of carbon would be 11.897, which is not in sufficiently close agreement with the actual determinations, and hence there can be little doubt that the author's value, 1.1050, is more correct.

The relative density of methane, calculated from its molecular weight, is 0.55376, which is lower than the general accepted value; but it is probable that the determinations were made with impure gas.

C. H. B.

Formation of Alkali Carbonates in Nature. By E. W. HILGARD (*Ber.*, 25, 3524—3630).—The author has determined quantitatively the amount of alkali carbonate which is formed when the solution of an alkali sulphate is treated with precipitated calcium carbonate in the presence of carbonic anhydride. Potassium sulphate, in solutions containing up to 1 gram per litre, is completely converted into potassium hydrogen carbonate. With stronger solutions, the percentage rapidly falls; so that in a solution containing 8 grams per litre, only 26.85 per cent. of the theoretical maximum

of potassium hydrogen carbonate is formed. With sodium sulphate, a similar result is obtained. A complete conversion of sodium sulphate into sodium hydrogen carbonate is obtained in solutions containing up to 0.8 gram per litre. If the solution of the carbonate is evaporated, 9/10ths of the carbonate is reconverted into sulphate.

The author points out the bearing of the results on the formation of alkali carbonates in the soil and on the action of gypsum when applied to the soil.

E. C. R.

Solutions of Sodium Silicates. By F. KOHLRAUSCH (*Ann. Phys. Chem.* [2], **47**, 756—764).—The author has studied the electrolytic conductivity of solutions of sodium silicate, Na_2SiO_3 , and of solutions containing the base and acid in the proportion Na_2O , 3.4SiO_2 , as well as some mixtures of the two with each other and with sodium hydroxide; and from his observations draws conclusions as to the constitution of the solutions examined. If a concentrated solution of the polysilicate is diluted, a long time elapses before the dilute solution attains chemical equilibrium; and, if soda is added to this diluted solution of the polysilicate, equilibrium is again only slowly reached.

The salt Na_2SiO_3 conducts better in dilute solution than equivalent solutions of any other salt. This is owing to hydrolytic decomposition of the salt into acid and base. The same phenomenon is apparent in the case of the polysilicate, only here the dilutions at which the conductivity is very high are much greater than before, as we should expect from the law of mass action. At an equivalent dilution of 100, the numbers obtained for solutions in which the proportion of acid to base varied, pointed to the ratio $2\text{SiO}_2 : 1\text{Na}_2\text{O}$ as being the superior limit of combination of silica with soda.

J. W.

Fusion of Calcium Carbonate. By H. LE CHATELIER (*Compt. rend.*, **115**, 1009—1011; compare this vol., ii, 117).—The author has repeated the experiments of J. Hall, using a steel tube with an internal coating of nickel. Chemically precipitated calcium carbonate was placed in the tube and heated at 1020° for about an hour. It was thus changed into a completely crystallised rod of calcium carbonate. As in the experiments under high pressures, it was clear that the carbonate had become pasty, but had not completely fused. It follows that the crystallisation of calcium carbonate may be the result of a high temperature only, without the intervention of a high pressure, a result directly opposed to that obtained by Joannis. The difference is doubtless due to the fact that in the author's experiments the tube was suddenly introduced into a furnace previously heated to the required temperature, whilst in the experiments of Joannis the temperature was raised more gradually. Similar differences are observed when sulphur or silica is heated rapidly or slowly, and in these cases the higher melting point observed is due to the formation of a less fusible isomeride during the process of heating. Possibly something of the same kind occurs in the case of calcium carbonate. Chalk crystallises under the same conditions as precipitated calcium carbonate, but calcite undergoes no change even at 1100° .

C. H. B.

Fusion of Calcium Carbonate. By A. JOANNIS (*Compt. rend.*, **115**, 1296—1298).—The author contends that the mass obtained by Le Chatelier (preceding abstract) by heating calcium carbonate at 1020° , not under pressure, had not really been fused, and that its crystalline condition was but little in advance of that of the precipitated carbonate. He has obtained similar results himself, but does not consider that fusion has taken place unless the mass is sufficiently hard to be polished and cut into thin sections. When in this condition, its sp. gr. is 2.57, which is almost identical with that of ordinary marble. Joannis points out that, according to Pictet's translation of Hall's memoir, the latter found that a minimum pressure of 173 atmos. is necessary to obtain complete fusion of calcium carbonate.

C. H. B.

Action of a High Temperature on Metallic Oxides. By H. MOISSAN (*Compt. rend.*, **115**, 1034—1036).—The author has constructed an electric furnace in which an electric arc impinges on a cavity in the middle of two blocks of lime (*Compt. rend.*, **115**, 1031—1033). Different temperatures are obtained by altering the strength of the current. In this paper he describes the effect of the arc on various oxides.

Calcium oxide, with a current of 50 volts and 25 ampères, rapidly becomes covered with brilliant, white crystals of the pure oxide. Similar results are obtained with lime of ordinary purity. With 50 volts and 100 ampères, crystallisation is much more rapid and abundant, and with 70 volts and 350 ampères, the calcium oxide melts completely, and, on cooling, solidifies to a confusedly crystalline mass. *Strontium oxide* crystallises at about 2500° , and at 3000° it melts to a transparent liquid, which, on cooling, solidifies to a confusedly crystalline mass. *Barium oxide* is completely liquid at 2000° , but seems to be stable even at 2500° . On cooling, it forms a mass of confused crystals with a beautifully crystalline fracture. *Magnesium oxide* crystallises less readily than calcium oxide. At about 2500° , it yields transparent crystals, and with 70 volts and 360 ampères, it melts to a transparent liquid. *Aluminium oxide*.—At about 2250° , pure alumina crystallises readily, and if mixed with a small quantity of chromium oxide, it forms ruby-red crystals, inferior, however, to those obtained by Fremy and Verneuil's method. With 25 volts and 75 ampères, the alumina not only melts but completely volatilises. *Chromic oxide*, with 55 volts and 30 ampères, melts to a black mass dotted with black crystals. *Manganese peroxide* melts and evolves oxygen, forming the monoxide, which absorbs some of the lime, and solidifies to a brown, crystalline mass on cooling. *Ferric oxide* melts and loses oxygen, forming the magnetic oxide, partly liquid and partly crystallised. *Nickel oxide* melts, and forms green crystals. *Cobalt oxide* melts somewhat rapidly, and forms rose-coloured crystals. *Titanic anhydride*, with 50 volts and 25 ampères, yields black, prismatic crystals of the monoxide; with 45 volts and 100 ampères, the monoxide melts in three minutes, and is partly dissociated and completely volatilised in eight minutes. *Cupric oxide* is completely decomposed at 2500° , and yields small masses of metallic copper and a crystallised compound of copper and calcium oxides.

Zinc oxide rapidly volatilises, and condenses in long, transparent, crystals at the mouth of the furnace and on the electrodes.

C. H. B.

Decomposition of Aqueous Vapour by Magnesium. By M. ROSENFELD (*Ber.*, 26, 59—60).—The experimental illustration of the combustion of magnesium in aqueous vapour devised by Moody (*Proc.*, 1891, 20) is substantially the same as that described by the author about ten years ago (*Ber.*, 15, 161); the same phenomenon can be more simply and elegantly shown by employing powdered magnesium instead of magnesium ribbon, but care has to be exercised in the heating, both of the metal and the water, otherwise the action is very violent.

F. S. K.

Monomagnesium Phosphate. By J. STOKLASA (*Zeit. anorg. Chem.*, 1, 307—312).—Pure magnesium oxide is dissolved in concentrated phosphoric acid (sp. gr. 1.4), and the solution evaporated on the water-bath until a crystalline pellicle is formed on the surface. The crystals are washed with ether until all the acid is removed, pressed, and dried in a current of air. The compound thus prepared has the composition $\text{MgH}_4\text{P}_2\text{O}_8 + 2\text{H}_2\text{O}$, and forms nodular aggregates of small crystals; it is non-hygroscopic, and, unlike the calcium salt, is not decomposed by water.

A. R. L.

Determination of the Atomic Weight of Cadmium. By W. S. LORIMER and E. F. SMITH (*Zeit. anorg. Chem.*, 1, 364—367).—Carefully purified cadmium oxide was dissolved in potassium cyanide, and the cadmium deposited electrolytically. From the ratio of the weight of the oxide to that of the metal, the atomic weight of cadmium was determined, the arithmetical mean of nine determinations giving the number 112.055 ($\text{O} = 16$). The highest result was 112.182, and the lowest 111.908.

H. C.

Possibility of the Existence of certain Metals in the Gaseous Condition at Temperatures below their Fusing Points. By W. SPRING (*Zeit. anorg. Chem.*, 1, 240—244).—By passing a current of hydrogen through a heated glass tube containing the volatile chlorides of copper or iron, a lustrous, metallic deposit is formed on the sides of the tube, which proves on examination to have a crystalline structure, whereas the metal obtained by similarly reducing the oxides is pulverulent and devoid of crystalline form. The chlorides of cobalt, nickel, chromium, uranium, and tungsten were also examined, and it was found that the reduced metal is crystalline in those cases only where the salts are volatile. Silver chloride is reduced at a temperature below that at which it volatilises, and here a spongy, crystalline mass of metal having no lustre is obtained. The author is of opinion therefore, that after the chlorine has been removed by the hydrogen from the volatile chlorides, the metals exist for a time in the gaseous condition. As, however, the metals mentioned are only volatile at temperatures far above those at which their chlorides suffer reduction, it is assumed that they exist in allotropic modifications, perhaps in the atomic condition. Schützenberger's view (*Abstr.*, 1891, 1429)

as to the existence of a volatile nickel hydrochloride may also be applied to other metals, but fails to throw any further light on the phenomena above described. When silver, platinum, or gold, in the form of leaf, is heated at 150° in a sealed tube with hydrochloric acid, the metal dissolves, but the chloride is subsequently reduced by the hydrogen formed during the interaction, and the metal reappears as microscopic crystals on the sides of the tube. It is possible in this case that even the platinum exists for some time in the liquid condition previously to assuming the crystalline form. A. R. L.

New Formation of Basic Sulphates of Copper. By L. MARCHLEWSKI and J. SACHS (*Zeit. anorg. Chem.*, **1**, 405—406).—If a saturated aqueous solution of copper sulphate is heated on a water bath with excess of dimethylaniline or diethylaniline, a bluish-green precipitate is formed which on examination is found to have the composition $6\text{CuO}, 2\text{SO}_3, 5\text{H}_2\text{O}$. It appears to be identical with the basic sulphate of copper already obtained in other ways by Reindel, Pickering, and Habermann. If copper sulphate solution is heated with quinoline, a salt of the composition $8\text{CuO}, 3\text{SO}_3, 10\text{H}_2\text{O}$ is obtained. This salt has not been before observed; it has a bright-green colour, and decomposes when heated to 200° . H. C.

Formation of Aluminium Sulphide. By A. H. BUCHERER (*Zeit. angew. Chem.*, 1892, 483—484).—The author has succeeded in economically preparing on the large scale aluminium sulphide, hitherto obtained by passing the vapour of carbon bisulphide over red hot alumina. A mixture of alumina and charcoal is strongly heated in an earthenware retort, and by means of an earthenware tube sulphur is from time to time introduced into the retort. The alumina is gradually completely converted into the corresponding sulphide.

The author thinks that aluminium sulphide may become of great importance in the metallurgy of aluminium. L. DE K.

Amorphous, Hydrated Ferric Oxide; Crystalline Ferric Hydroxide; Potassium and Sodium Ferrites. By J. M. VAN BEMMELEN and E. A. KLOBBE (*J. pr. Chem.* [2], **46**, 497—529).—Rousseau claims to have obtained crystallised ferric hydroxide, $\text{Fe}_2\text{C}_3, \text{H}_2\text{O}$, by heating hydrated ferric oxide in molten alkali salts (Abstr., 1888, 917, 1034, 1252), and by decomposing ferric oxychloride by water (Abstr., 1890, 1063). Brunck and Graebe obtained the same compound (Abstr., 1881, 126). The results of the authors' reinvestigation of this matter are as follows:—(1.) The hydrous ferric oxide obtained by decomposing potassium nitroprusside, or Roussin's salt (compare Pavel, Abstr., 1883, 297) with alkali hydroxides, and gelatinous hydrated ferric oxide which has been exposed to a low temperature, are amorphous, and of inconstant composition. (2.) Continued heating with a strong solution of potassium or sodium hydroxide converts ferric oxide into a ferrite which is partially soluble and gradually becomes crystalline. In potassium hydroxide solution, the crystals are at first rhombic (?) plates, but as

the heating is continued and the water expelled they become regular octahedra, which are also formed when ferric oxide is heated in fused potassium carbonate or chloride. In sodium hydroxide, the crystals are, at first, crossed prisms, but afterwards hexagonal plates, sometimes becoming rhombohedral and spherical, or long needles; the same are formed when ferric oxide is heated in fused sodium carbonate or chloride. All these crystals have the composition $\text{Fe}_2\text{O}_3 \cdot \text{K}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot \text{Na}_2\text{O}$, respectively. (3.) These crystals (with the exception of the hexagonal plates) are decomposed by water, assuming at first a pseudocrystalline form and then becoming amorphous, hydrated ferric oxide. (4.) The hexagonal sodium ferrite yields $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ when treated with water; this has the same crystalline form, transparency, and optical properties as the original ferrite; it is not hygroscopic, but begins to lose water below 100° , whereas göthite can be heated to 300° without losing water. (5.) Rousseau's crystalline ferric hydroxide (*loc. cit.*) is, in the authors' opinion, a pseudocrystalline hydrated ferric oxide formed by the decomposition of a ferrite by water (compare 3).

A. G. B.

Action of Metallic Molybdenum and Tungsten on Solutions of Silver, Gold, and other Metals. By E. F. SMITH (*Zeit. anorg. Chem.*, **1**, 360—363).—Metallic molybdenum precipitates silver from a solution of silver nitrate, the solution becoming turbid through separation of molybdic acid. If a solution of silver oxide or chloride in ammonia is taken, the turbidity is avoided. The reaction is quantitatively complete, one atom of molybdenum precipitating six of silver. In the case of the chloride, the solution evidently must contain the hexachloride, MoCl_6 , and this is also formed when molybdenum precipitates gold from auric chloride, a quantitative reaction in which one atom of molybdenum precipitates two of gold. The colour of the resulting solution in the two last instances is a dark-brown. Tungsten acts towards silver and gold solutions very like molybdenum, the action in the case of gold being, however, somewhat slower. Neither metal has any action on neutral, alkaline, or acid solutions of lead nitrate. Molybdenum reduces neutral mercuric chloride at once to mercurous chloride, and eventually to metallic mercury. Tungsten only acts slowly and forms mercurous chloride. Both metals precipitate copper from solutions of copper salts, but the action is not a complete one. Solutions of bismuth and cadmium are unaffected by either metal, and platinum, palladium, and rhodium chlorides only undergo partial reduction.

H. C.

A Crystalline Alloy of Iron and Tungsten. By T. POLECK and B. GRÜTZNER (*Ber.*, **26**, 35—38).—A lump of iron-tungsten alloy, obtained by an electrolytical method from Bohemian wolframite, was found to consist of a crystalline ground-mass, of the composition $\text{Fe}_2\text{W}_3\text{C}_3$, in the crevices of which were small crystals of the composition FeW_2 . The latter form trigonal prisms which belong to the hexagonal system, and are either trapezohedral-tetartohedral, or else rhombohedral-hemihedral and hemimorphous along the primary

axis. Both the crystals and the crystalline matrix are silver-grey, very heavy, and very hard—about as hard as corundum.

C. F. B.

Action of Potassium and Sodium Hydroxides on Antimony Trioxide. By H. CORMIMBOEUF (*Compt. rend.*, 115, 1305—1307).—

When a solution of 2 parts of potassium hydroxide in an equal quantity of water holding in suspension 1 part of precipitated antimony trioxide, is boiled for a few minutes, rhombic prisms that act strongly on polarised light are formed. They have the composition $K_2O, 3Sb_2O_3$, are easily decomposed by cold water, and, when exposed to air, rapidly absorb carbonic anhydride with formation of potassium carbonate and separation of antimony oxide.

If to a boiling solution of potassium hydroxide in its own weight of water, antimony oxide is added in successive small portions until it ceases to dissolve, and the liquid is allowed to cool, the compound $K_2O, 3Sb_2O_3, 3H_2O$ crystallises in rectangular lamellæ which act on polarised light and show longitudinal extinction.

When water is added gradually to the anhydrous or hydrated triantimonite, the salt is decomposed with separation of prismatic antimony oxide, but as soon as the water, by decomposition of the salt, has become charged with 5 per cent. of potassium hydroxide, octahedral antimony oxide is formed, and when the proportion of hydroxide in solution reaches 20.9 per cent., decomposition ceases. The octahedral oxide obstinately retains 0.6—0.2 per cent. of alkali.

If a boiling solution of 1 part of sodium hydroxide in 2 parts of water is saturated with antimony trioxide, and the liquid is then poured into a large quantity of boiling water, and the mixture is filtered, the liquid as it cools, deposits quadratic tables which adhere strongly to the glass. They have the composition $Na_2O, Sb_2O_3 + 6H_2O$, and recrystallise from pure water in octahedra with a square base, but with the same composition. This salt has already been described by Terreil, who obtained it in a somewhat different manner.

If a boiling solution of 1 part of sodium hydroxide in 2 parts of water is mixed with successive quantities of antimony oxide until it ceases to dissolve, and the liquid is allowed to cool, monoclinic needles of the composition $2Na_2O, 3Sb_2O_3 + H_2O$ separate.

When a similar solution of sodium hydroxide is boiled with an excess of antimony oxide, the liquid, whilst still warm, deposits rhombic tables of the composition $Na_2O, 2Sb_2O_3$. If the liquid, instead of being boiled, is heated with the excess of antimony oxide at 100° , it deposits at that temperature rectangular tables of the composition $Na_2O, 3Sb_2O_3$.

All the sodium antimonites alter rapidly in moist air, with formation of sodium carbonate and separation of amorphous antimony oxide. Pure water, either cold or hot, decomposes them with separation of prismatic antimony oxide, which obstinately retains 0.55—0.64 per cent. of alkali. The sesquiantimonite, diantimonite, and triantimonite undergo no alteration in contact with solutions of sodium hydroxide containing respectively 94.3, 183.6, and 113.2 grams per litre.

It is noteworthy that sodium hydroxide yields three antimonites, all of which yield antimony oxide in the crystalline form of valentinite when they are decomposed by water, whereas potassium hydroxide yields only one antimonite, but this, when treated with water, yields antimony oxide crystallised in the forms of both valentinite and senarmonite.

C. H. B.

Action of Bismuth on Hydrochloric acid. By A. DITE and R. METZNER (*Compt. rend.*, 115, 1303—1305).—Bismuth is not attacked by gaseous hydrogen chloride at the ordinary temperature, nor at any temperature up to the softening point of glass. In contact with a dilute or concentrated solution of the acid, bismuth liberates no hydrogen either under ordinary pressure or in a vacuum, nor even after the bismuth has been in contact with a solution of some metallic chloride which can deposit a thin layer of some other metal on its surface. Sometimes bismuth is found in the solution, although no gas has been liberated, but this only happens when oxygen has not been entirely excluded.

When left in contact with aerated water free from carbonic anhydride, bismuth, after a long time, becomes covered with small crystals of the hydrated oxide, but no bismuth goes into solution.

It follows that bismuth, like antimony, is not attacked by hydrochloric acid except in presence of oxygen, and the readiness with which arsenic, antimony, and bismuth separately dissolve in the acid in presence of oxygen is in intimate relation with their respective heats of oxidation.

C. H. B.

Ammoniacal Derivatives of Ruthenium Chloride. By A. JOLY (*Compt. rend.*, 115, 1299—1301).—Anhydrous ruthenium chloride rapidly absorbs dry ammonia at the ordinary temperature with considerable development of heat, and absorption is only complete when the substance is cooled to 0°. The product has then the composition $\text{Ru}_2\text{Cl}_6 + 7\text{NH}_3$, and if gradually mixed with water, it partially dissolves, forming an intense violet-red liquid, but solution is only complete if the water is saturated with ammonia. Similarly, if finely divided anhydrous ruthenium chloride is projected in successive small quantities into a solution of ammonia saturated at a low temperature, and the mixture is heated for some time at 40°, a very deep red solution is obtained which, when sufficiently concentrated, deposits small, crystalline lamellæ of the composition $\text{Ru}_2\text{Cl}_4(\text{OH})_2, 7\text{NH}_3, 3\text{H}_2\text{O}$. The crystals are brown with a metallic lustre by reflected light, and yellow by transmitted light; the solution is red by transmitted light, and has a violet tinge by reflected light. 1 part of the compound in 10,000 parts of water has an intense red colour, and even 1 part in 5,000,000 parts of water has a distinct rose colour. The dry salt is stable when exposed to light, but its solutions decompose with precipitation of the brown sesquioxide. Decomposition is rapid when the solution is boiled, and intermediate products are formed either by loss of ammonia or by progressive substitution of the elements of water for chlorine.

When concentrated hydrochloric acid is added to concentrated solutions of the ammoniacal hydroxychloride, the compound



separates as a brown precipitate. When dissolved in water, it forms a yellow solution, but as the proportion of water is increased, the colour changes to red. A small quantity of ammonia or other alkali changes the colour at once to reddish-violet. By double decomposition with silver nitrate in acid solution, the hydrochloride of the hydroxychloride yields readily crystallisable salts, forming yellow solutions which become red on the addition of a base.

The red coloration that appears on boiling an ammoniacal solution of the nitroso-oxychloride is due to the formation of the ammoniacal hydroxychloride now described, and is not due to the reproduction of the original nitrosochloride by loss of ammonia. C. H. B.

Mineralogical Chemistry.

Artificial Production of Rutile. By L. MICHEL (*Compt. rend.*, 115, 1020—1021).—When an intimate mixture of titaniferous iron ore 1 part, and pyrites 2·5 parts, is heated in a graphite crucible at about 1200° for several hours and allowed to cool, a crystalline mass is obtained which has all the chemical and physical properties of pyrrhotine.

The mass is full of cavities, to the walls of which are attached elongated, quadratic prisms of rutile, identical in every respect with the natural crystals. They are uniaxial and positive, have a deep blue colour and adamantine lustre, are infusible before the blowpipe, and are not attacked by acids; hardness = 6; sp. gr. = 4·28.

The pyrrhotine has the composition Fe_8S_9 , and is in crystalline masses with a lamellar texture and a bronze-yellow colour; hardness 4; sp. gr. 4·5. It is slightly magnetic. C. H. B.

Minerals from Lower Silesia. By B. KOSMANN (*Jahrb. f. Min.*, 1893, i, Ref. 9—10; from *Zeit. deutsch. geol. Ges.*, 42, 794—796).—Chrome-iron ore occurs in a serpentine in a vein 7 metres in thickness at Tampadel. The ore contains inclusions of magnetite and spinel. Analysis gave results varying within the following limits:—

Cr_2O_3 .	MgO .	SiO_2 .	FeO .	Al_2O_3 .
35—42	14—16	4—6	18—22	18—22

A specimen of ore from the Bergmannstrost mine consists of iron pyrites, arsenical pyrites, blende, and tetrahedrite with dolomite. In a cavity in the mass there are twin crystals of bournonite covered with dolomite and barytes. B. H. B.

Palygorskite. By P. ZEMIATSCHEVSKY (*Jahrb. f. Min.*, 1893, i, Ref. 33—34; from *Bibl. géol. Russ.*, 6, 90).—The name of palygorskite was given in 1860 by Savtschenkoff to a fibrous mineral resembling asbestos from the government of Perm. Since that date the mineral has been found at various localities in Russia in Permian and Tertiary beds, and has repeatedly been analysed. A specimen from Nijni-Novgorod was analysed by the author with the following results:—

H ₂ O.	CaO.	MgO.	Al ₂ O ₃ .	SiO ₂ .	CO ₂ .
19·68	10·52	8·30	13·93	44·40	3·17

B. H. B.

Composition of Melilite. By G. BODLÄNDER (*Jahrb. f. Min.*, 1893, i, Mem. 15—21).—The author has analysed some good specimens of melilite from Monte Somma with the following results:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
41·34	10·37	4·29	33·84	5·79	1·13	3·45	0·08	100·29

Comparing his results with the published analyses of artificial and natural crystals of melilite, the author concludes that the optically negative melilites are metasilicates of the formula $\text{SiO}_3\text{R}''$, isomorphously mixed with the aluminate $\text{R}'''_2\text{O}_4\text{R}''$, whilst in the optically positive melilites, the aluminate $\text{R}'''_2\text{O}_6\text{R}'''_3$ is in isomorphous mixture with the silicate $\text{SiO}_3\text{R}''$. In conclusion, the author brings forward arguments disproving Vogt's theory (*Abstr.*, 1892, 1410) that melilite is a mixture of ghlenite and akermanite.

B. H. B.

Pholidolite from Sweden. By G. NORDENSKJÖLD (*Jahrb. f. Min.*, 1893, i, Ref. 20—21; from *Geol. Fören. Förhandl.*, 12, 348).—At Taberg, in Wermland, pholidolite occurs in greyish-yellow, micaceous laminae, having a sp. gr. of 2·408. Analysis gave the following results:—

SiO ₂ .	Al ₂ O ₃ .	MgO.	FeO.	MnO.	K ₂ O.	H ₂ O.	Total.
49·78	6·31	27·94	4·08	0·12	5·93	5·49	99·65

Other minerals occurring in the same cavities are:—garnet, diopside, epidote, apatite, titanite, magnetite, calcite, galena, and chlorite.

B. H. B.

Existence of the Diamond in the Meteoric Iron of the Cañon Diablo. By C. FRIEDEL (*Compt. rend.*, 115, 1037—1041).—A specimen of meteoric iron from the Cañon Diablo was found by Le Bel to contain diamonds, and the specimen found by Eckley Coxe (*Abstr.*, 1892, 947) was cut in two, and a portion weighing 34 grams was treated successively with hydrochloric acid, aqua regia, and hydrofluoric acid. The residue contained minute rounded grains, which had all the properties of carbonado, and which when heated to redness in oxygen formed carbonic anhydride. There can, therefore, be no doubt of the existence of diamonds in the meteorite. The diamonds were not uniformly distributed in the specimen examined, but were

concentrated in and about nodules of iron sulphide and phosphide. The sp. gr. of the grains was slightly higher than 3·3; the sp. gr. of carbonado varies between 3·0 and 3·41. C. H. B.

Hepatic Mineral Water and Mud of the Valle del Gallo.

By A. AGRESTINI (*Gazzetta*, 22, ii, 287—298).—The hepatic spring of the Valle del Gallo is distant about 12 kilometres from Urbino, and 24 from Pesara. Its waters are reputed to have considerable medicinal value. The water has a strong odour of hydrogen sulphide, and issues at a temperature of 14·0—14·2°; its sp. gr. = 1·00274 at 24°; 1000 grams at 14° and 760 mm. contain the following constituents:—

CO ₂ (free).	H ₂ S (free).	Oxygen.	Nitrogen.	
70·212 c.c.	43·06 c.c.	0·625 c.c.	17·41 c.c.	
CaH ₂ (CO ₃) ₂ .	MgH ₂ (CO ₃) ₂ .	NaHCO ₃ .	NH ₄ HCO ₃ .	
0·5228 gram	0·0089 gram	0·0262 gram	0·0043 gram	
FeH ₂ (CO ₃) ₂ .	CaSO ₄ .	MgSO ₄ .	Na ₂ SO ₄ .	Na ₂ SiO ₃ .
0·0017 gram	1·5558 grams	0·4501 gram	0·0330 gram	0·0012 gram
AlPO ₄ .	KCl.	NaCl.	NaHS.	SiO ₂ (free).
0·0005 gram	0·0281 gram	0·1542 gram	0·0048 gram	0·0437 gram

0·1071 gram of organic matter and traces of manganese and arsenic are also present. The solid residue from 1000 grams dried at 180° weighs 2·7923 grams.

The mud taken from the hole in which the water collects is applied externally to cases of skin disease, etc., with good results. After drying at 125°, it has the following percentage composition:—

(NH ₄) ₂ SO ₄ .	CaSO ₄ .	Ca ₃ (PO ₄) ₂ .	CaCO ₃ .	MgCO ₃ .	NaCl.
0·199	1·470	0·181	25·342	6·044	0·011
K ₂ O.	Na ₂ O.	MgO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	SiO ₂ (comb.).
3·356	2·345	2·964	11·676	6·573	23·390
					SiO ₂ (free).
					9·184
S (free).	BaSO ₄ . Mn, As.			Organic matter and H ₂ O.	
0·458	traces			6·253	

W. J. P.

Physiological Chemistry.

Influence of Acids and Alkalis on the Determination of the Osmotic Pressure in relation to the Red Blood Corpuscles. By H. J. HAMBURGER (*Rec. Trav. Chim.*, 11, 61—75).—Acids and alkalis modify the permeability of the blood corpuscles for their different constituents. Acids and alkalis act in opposite ways; the action of an acid can be neutralised by an alkali, and *vice versa*.

The permeability of the red corpuscles for hæmoglobin is modified in the following way:—After being acted on by acids, they lose their colouring matter in a solution of sodium chloride, but it must be stronger than was necessary before such action took place; they keep their pigment after the action of an alkali in a more dilute solution of sodium chloride than before this action.

Thus, the red corpuscles begin to lose their hæmoglobin in a 0.56 per cent. solution of sodium chloride; but, after the action of a dilute acid, the strength of the solution must be increased to 0.67 per cent., and, after the action of dilute alkali, it must be diminished to 0.51 per cent.

When the attractive force for water (osmotic pressure) is determined, it is necessary to take account of such facts, otherwise the results will be valueless.

Errors can be avoided by carefully neutralising, and by determining the attractive force for water in the neutral fluid. There is, however, still to be subtracted from the number found the attractive force for water of the acid or alkali employed in neutralisation, and, further, to take into account the dilution which results from this operation.

W. D. H.

Occurrence of Glycogen in Blood. By HUPPERT (*Chem. Centr.*, 1892, ii, 873; from *Centr. Physiol.*, 6, 394).—The author confirms the presence of glycogen in blood. It seems always to be present, but in quantities varying with the kind of blood, and the amount is always very small: ox blood contains 5–10 milligrams per litre.

Glycogen occurs invariably in pus and in larger amounts than in blood; the pus corpuscles contain it in larger amount than does the serum.

A. J. G.

Acid Reaction of Muscle. By F. A. MEYERHOLD (*Chem. Centr.*, 1892, ii, 835–836; from *Sitzber. Physik.-med. Soc. Erlangen*, 24, 128–155).—It seems probable that living quiescent muscle contains a small quantity of lactic acid, or, at least, of some substance having an acid reaction. In an indifferent liquid, such as distilled water or physiological salt solution, where the disturbing influence of putrefaction is prevented by the action of cold (not by antiseptics), the muscle yields, after a time, a certain amount of acid. This amount is increased by raising the temperature to 45°, but is diminished by cooling. Heating to the boiling point suspends the process for a short time, but does not terminate it, neither is it destroyed by alcohol. The author then points out that the amount of lactic acid found is incompatible with the theory that it is derived from the glycogen in the muscle.

A. J. G.

Accumulation of Potassium Bromide in the Organism. By C. FÉRÉ and L. HERBERT (*Compt. rend. Soc. Biol.*, 1891, 769–771, 807–809).—In man, potassium bromide accumulates in the organs, especially in the brain, liver, and kidneys.

Two cases of epileptics are recorded; they had been treated with this drug for long periods. The amounts found per cent. *post mortem* are given in the following table.

	Case 1.	Case 2.
Brain	0·073	0·090
Lung	0·082	0·156
Liver	0·104	0·137
Spleen	0·133	0·210
Kidney	0·100	0·216
Pancreas	0·043	—
Muscles	0·062	0·160
Cartilages	0·041	0·170
Bones	0·087	0·240
Blood	—	0·270
Testes	—	0·280

These cases show that there is an accumulation of the salt in the tissues; and in the case (No. 2) where the treatment was continued longest (five years), the tissues, where the accumulation is greatest, are those where the nutrition is slow, like the bones and cartilages.

Similar observations were made on animals, rabbits and guinea-pigs, the salt being given subcutaneously. After a few days the animals died, and their bodies were incinerated. Considerable quantities of the salt were found in the ash, showing that its elimination during the first few days is slow. The individual organs were not investigated.

W. D. H.

Nutritive Value of Asparagine. By S. GABRIEL (*Zeit. Biol.*, **29**, 115—124). **Remarks on the above.** By K. VOIT (*ibid.*, 125—128).—The first of these papers is a criticism of that recently published by Politis (this vol. ii, 27). Voit's remarks point out that Gabriel does not contradict Politis in the statement that asparagine is not a proteid-sparing food, but that he merely states that asparagine has a beneficial effect by promoting the absorption of starchy food.

W. D. H.

Metabolism in Diabetes Mellitus. By F. VOIT (*Zeit. Biol.*, **29**, 129—146).—Dieting experiments on diabetic patients, compared with similar ones on healthy people, do not show any very great difference in the general course of metabolic activity. More proteid is, however, used by diabetics, carbohydrate not being available as a proteid-sparing food. Experiments on gas exchange also show that more fat undergoes combustion in diabetics as compared with the normal.

W. D. H.

Behaviour of Galactose in Diabetics. By F. VOIT (*Zeit. Biol.*, **29**, 147—150).—Although galactose will not increase the hepatic glycogen (C. Voit and others, *Abstr.*, 1892, 902), it causes an increase of the sugar in diabetes. The experiment was made on the same patient as was formerly experimented on in connection with lactose (F. Voit, *ibid.*, 903). The result obtained was the same as with lactose, and is capable of a similar explanation.

W. D. H.

Occurrence of Ammonia in the Stomach Contents. By T. ROSENHEIM (*Chem. Centr.*, 1892, ii, 749; from *Centr. Klin. Med.*, **13**, 817—819).—The stomach contents are filtered, the proteids removed

by acetic acid and tannin, and the estimation of the ammonia then proceeded with according to Schloesing's method. In healthy subjects, ammonia was found in all phases of digestion and after the ingestion of the most varied foods; the amount being, as a rule, from 0.1 to 0.15 per mille. In many diseases of the stomach, the values still lie within these limits, but occasionally are found to be higher.

It is not possible to estimate the amount of ammonium chloride in the stomach contents, but it must be taken into consideration when estimating the total chlorine: hitherto it must have been calculated as hydrochloric acid.

A. J. G.

Uroerythrin and Hæmatoporphyrin in Urine. By L. ZOJA (*Chem. Centr.*, 1892, ii, 748—749; from *Centr. med. Wiss.*, 1892, 705—706).—Uroerythrin is characterised by (1) its absorption spectrum—two bands of about equal intensity at about λ 550—525— λ 510—484, the interspace also showing absorption; (2) the great sensitiveness of its solution to light; (3) the green coloration which it gives with alkalis; (4) the properties of the precipitates with urates and with salts of lead, potassium, and barium. Uroerythrin probably occurs in the urine as a salt (sodium salt) in combination with urates.

Hæmatoporphyrin is characterised by (1) the spectra of its acid and alkaline solution; (2) the properties of its metallic compounds; (3) the evolution of pyrroline when heated in the dry state; (4) the scatole-like odour and formation of a uribilinoïd substance when treated with zinc and hydrochloric acid; (5) a reaction resembling Gmelin's with nitric acid. Hæmatoporphyrin from urine is identical with that obtained by the action of reducing agents on hæmatin. McMunn's hæmatoporphyrin is, at least as a rule, a mixture of urobilin and hæmatoporphyrin. Hæmatoporphyrin probably occurs as such in the urine; it is found in the most varying proportions.

A. J. G.

Behaviour of Xylenes in the Organism. By A. CURCI (*Chem. Centr.*, 1892, ii, 538; from *Ann. Chim. Farm.*, 16, 3).—The xylenes show a double action, an irritant action such as is characteristic of phenols and the paralysing action characteristic of aromatic hydrocarbons. The paralysing action is shown most strongly by orthoxylene, less strongly by metaxylene, whilst paraxylene occupies a mean position between the other two. The irritant action is strongest with the para-compound, less with the ortho-, and still less with the meta-compound. The explanation of the irritant action is, that the xylenes suffer partial conversion in the organism into the xylenols, but to an unequal extent, the para-compound being the most affected.

A. J. G.

Influence of the Carboxyl Group on the Toxic Action of Aromatic Compounds. By M. NENCKI and H. BOUTMY (*Chem. Centr.*, 1892, ii, 655—656; from *Arch. exp. Path. Pharm.*, 30, 300—310).—Many poisonous aromatic compounds become relatively non-poisonous when the carboxyl group is introduced into the molecule, seemingly through the greater stability thus induced. Thus

benzoic acid is less poisonous than benzene, and the same seems to be true as regards naphthalenecarboxylic acid and naphthalene. The same relations hold for the hydroxylated derivatives of benzene and their carboxylic acids; thus whilst orthamidophenol is less poisonous than aniline, ortho- and para-amidosalicylic acids are harmless. Orthoxycarbanilcarboxylic acid is less poisonous than oxycarbanil; it passes through the organism without causing discomfort and can be detected in the urine. Malonanilic acid is a less powerful poison than acetanilide, of which it may be regarded as a carboxylated derivative; it can pass into the urine, and the ingestion of its sodium salt is not followed by an increase in the ethereal hydrogen sulphates in the urine. A like relation is observed between paraphenacetinic acid and phenacetine.

The sulphonic group in replacing hydrogen seems to exert an influence on physiological action resembling that described above for the substitution of the carboxyl group for hydrogen. A. J. G.

Physiological Effect of Opium Smoke. By N. GRÉHANT and E. MARTIN (*Compt. rend.*, 115, 1012—1014).—Opium smoke produced at a temperature of 250°, as is done by actual smokers (this vol., i, 226), has scarcely any effect on a dog. It is without influence on the energy of the contractions of the heart, and the only difference observable is that when anæsthesia is produced by means of a mixture of chloroform and alcohol, the period of agitation at the beginning is shorter with an animal that has been submitted to the action of opium smoke than with one that has not. It is clear that there is a distinct difference between the central nervous systems of the dog and man.

One of the authors smoked successively 20 pipes containing altogether about 4 grams of *chandoo* or prepared opium. After the fourth pipe, frontal headache began, and after the sixth, the headache became general; at the tenth, vertigo set in and continued until the end of the experiment. Half an hour after the smoking stopped, the headache and vertigo began to decrease, and at the end of an hour had quite disappeared. The curve of respiration at the end of the experiment had a somewhat smaller amplitude than at the beginning, and the pulsations of the heart were rather less frequent.

C. H. B.

Toxicity of certain Mineral Salts. By C. RICHET (*Compt. rend. Soc. Biol.*, 1891, 774—775).—The salts used were bromides, chlorides, and iodides of lithium, potassium, and rubidium. The results show that the toxic dose is proportional to the molecular weight of the salt and not to its absolute weight. A molecule of rubidium iodide, which weighs 207, is as poisonous as a molecule of lithium chloride, which only weighs 42.

Microbes show great resistance to the toxic action of potassium salts. Mercury is the metallic poison which is most active; it is weight for weight ten times more toxic than copper. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

An Organised Ferment from Cherry Tree Gum. Pectinose. By F. GARROS (*J. Pharm.* [5], 26, 535—537).—Cherry tree gum left in a sterilised flask liquefies after some time, and a yeast-like microbe is found therein, which is more active in presence of ammonium tartrate and is rendered inactive on the addition of hydrochloric acid (5 per cent.). This ferment liquefies plum and cherry tree gums but not gum arabic. The author states that, whereas the precipitate yielded by ferric sulphate with arabin is insoluble in potassium hydroxide solution, that afforded by pectin dissolves at once, and these substances are further distinguished since strong solutions of arabin are rendered insoluble by pure concentrated sulphuric acid, whilst pectin is converted into a sugar which he calls pectinose; this sugar may also be made from beet husks by boiling them with dilute hydrochloric acid for some time, and isolated by precipitating with basic lead acetate and then treating the lead compound with hydrogen sulphide. T. G. N.

Exchange of Carbonic Anhydride and Oxygen between Plants and the Atmosphere. By T. SCHLOESING, JUN. (*Compt. rend.*, 115, 1017—1020).—Woolly feather-grass was sown on quartzose sand early in July, and the ratio of carbonic anhydride decomposed to oxygen set free was determined from time to time between the date of sowing and September 6th, when the crop, which was well developed, was cut.

	Aug. 13.	Aug. 18.	Aug. 26.	Sept. 1.	Sept. 6.
$\frac{\text{CO}_2 \text{ disappeared}}{\text{O liberated}} =$	0.87	0.88	0.88	0.91	0.89

It will be observed that the ratio CO_2/O is distinctly less than unity and remains practically constant throughout the whole period of vegetation.

The composition of the organic portion of the crop shows that it contains more hydrogen than would form water with the oxygen which it also contains. It seems, therefore, that the plant itself eliminates oxygen in some form, and possibly, as suggested by Dehérain and Maquenne in a similar case, it is eliminated as carbonic anhydride.

On the other hand, the composition of the plant, when compared with the measurements of carbonic anhydride and oxygen, shows that it has derived some oxygen through its roots from the oxy-salts present in the soil. C. H. B.

Supposed Presence of Albumin in the Walls of Vegetable Cells. By S. L. M. MOORE (*Chem. Centr.*, 1892, ii, 872—873; from *J. Linn. Soc.*, 29, 241).—The substance in the cell walls which gives the reactions for albumin is not albumin, at least not a peptonisable albumin, neither is it tyrosine. Krasser's list of the substances which

react like proteïds is not complete, as the three reactions which the cell walls give (Millon's, Raspail's, the xanthoprotein reaction) are also given by a solution of catechu, as are other reactions shown by the cell walls. The behaviour of lignified cell walls to some reagents shows the presence of an iron-greening dye (probably a tannin) in them. The fact that the cell walls are not able to take up carmine and aniline-blue is not reconcilable with their containing albumin, but no form of tannin takes up carmine, and iron-greening tannins are not coloured by aniline-blue. The cell nucleus also probably contains an iron-greening tannin.

It is doubtful whether proteïds occur in the milky juice of the fig, as the proteïd reactions which this gives may also be due to an iron-greening tannin.

A. J. G.

Cork and Suberin. By C. VAN WISSELINGH (*Chem. Centr.*, 1892, ii, 516; from *Nederl. Tijdschr. Pharm. Chem. Toxicol.*, 1892, 220).—Cork does not contain cellulose. The violet coloration which it gives with zinc chloride and iodine solution is due to phellonic acid. Cork contains several fusible substances, which are soluble in chloroform; these consist of glyceryl salts of the various acids. From the saponification products of these substances, *phellonic acid*, melting at 95°, a second acid melting at 60–70°, and several other less well characterised acids were obtained. The fusible substances mentioned above are enveloped in others which are not fusible or soluble in chloroform, but dissolve readily in cold aqueous potash.

A. J. G.

Ethyl Alcohol in Oil of Roses. By T. POLECK (*Ber.*, 26, 38–39).—Oil prepared in Germany, on the spot where the roses were grown, was found to contain no ethyl alcohol. That previously found in other samples must have been formed by fermentation taking place in the leaves during their transport to the factory.

C. F. B.

Occurrence of Thymol in the Ethereal Oil of Mosula Japonica. By Y. SHIMOYAMA and H. ONO (*Chem. Centr.*, 1892, ii, 618; from *Apoth. Zeit.*, 7, 439–440).—Dried plants of the Japanese labiate *Mosula Japonica*, on distillation with water, yielded 2.13 per cent. of a brownish-red, ethereal oil of feeble, thymol-like odour; it was lævorotatory, and had a sp. gr. = 0.820 at 17.5°. On agitation with strong aqueous soda, an oily liquid boiling at 170–180°, and smelling like cymene, was obtained, whilst the aqueous solution, when saturated with carbonic anhydride, yielded thymol.

A. J. G.

Loss of Nitrogen in Manures. By A. MUNTZ and A. C. GIRARD (*Compt. rend.*, 115, 1318–1321).—The authors have estimated the loss of nitrogen that takes place in the stable before the manure is put into a heap, by estimating the nitrogen introduced in the forage and the litter, also that found in the products, such as milk, wool, &c., and in the manure at the time that it was removed. The difference is taken as the loss of nitrogen occurring in the stable. The results were as follows:—

	16 horses. kilos.	10 cows. kilos.	25 sheep. kilos.
Nitrogen in the forage.....	43·795	90·116	14·548
„ in the litter (straw)...	8·642	6·532	0·115
„ in the animal products	0·000	17·742	0·900
„ in the manure.....	39·860	50·108	6·464
„ lost.....	12·577	28·798	7·299
„ lost per cent. of nitrogen supplied.....	28·7	31·9	50·2

When the manure is in a heap and is left to itself, the losses are much smaller; with horse manure, after four months, the loss is 23·1 per cent. of the initial nitrogen, and 20·9 per cent. of the nitrogen consumed in the fodder; with cows' manure, after three months, 2·39 per cent. of the initial nitrogen, and 10·8 per cent. of the nitrogen consumed in the fodder; and with sheep's manure, after six months, the loss is 11·3 per cent. on the first basis, and 5·0 per cent. on the second.

The relatively great loss of nitrogen in the stable is attributable to the rapid fermentation of the urine; the solid excreta retain their nitrogen longer. The loss is somewhat greater in summer than in winter; in the case of cows, the loss is 52·7 per cent. of the original nitrogen in June and July, and only 44·7 per cent. in January, February, and March. The loss is slightly less when the fodder is green than when it is dry, probably because in the first case the excreta contain more moisture, and the tension of the ammonia is lower. It is not affected to any important extent by increasing the bulk of the litter.

C. H. B.

Fermentation of Manure. By A. HÉBERT (*Compt. rend.*, 115, 1321—1323).—The author has investigated the changes which the nitrogen undergoes during the fermentation of straw at 55° in the absence of excess of oxygen. The straw was powdered, moistened with 5 per cent. solutions of potassium and ammonium carbonates, and inoculated with a small quantity of liquid manure. Methane and carbonic anhydride were given off, and after three months the straw had lost nearly half its weight. In all cases, there was a reduction in the ammoniacal nitrogen, and an increase in the organic nitrogen, as in Dehérain's experiments. The total loss of nitrogen is considerable, but neither in the experimental flasks nor in the case of manure heaps does this loss take place in the form of ammonia. If a manure is too dry, the methane fermentation is greatly retarded, and it follows that moistening the manure not only promotes this fermentation, but reduces the risk of loss of ammonia.

The nitrogen which is lost escapes in the free state, and hence the practice of adding iron sulphate, calcium sulphate, &c., with a view to prevent loss of ammonia, is useless if the manure is kept sufficiently moist.

C. H. B.

Analytical Chemistry.

Quantitative Separation and Estimation of Chlorine, Bromine, and Iodine. By C. FRIEDHEIM and R. J. MEYER (*Zeit. anorg. Chem.*, **1**, 407—422).—After a critical examination of the various methods that have been proposed for the estimation of mixed chlorides, bromides, and iodides, the authors have adopted the following process. The mixture is introduced into a small retort of special form and mixed with potassium dihydrogen arsenate and dilute sulphuric acid. The iodine separates, and can be distilled over into a receiver containing potassium iodide solution, preferably by means of a current of steam. It is then titrated in the ordinary way with thiosulphate solution. The residue in the retort is allowed to cool, and then mixed with a concentrated solution of potassium dichromate. On heating, the whole of the bromine is liberated, and is collected in the receiver, which has been again charged with potassium iodide solution. The iodine set free is determined as before with thiosulphate solution. The chloride which remains in the retort with the excess of dichromate is determined gravimetrically by precipitation with silver nitrate, after the solution has been acidified with nitric acid. The test analyses show that the method gives very fair results.

H. C.

Direct Quantitative Separation of Chlorine and Iodine. By P. JANNASCH and K. ASCHOFF (*Zeit. anorg. Chem.*, **1**, 248—250).—The method depends on the insolubility of thallium iodide in aqueous alcohol, and the solubility of thallium chloride in solutions of ammonium salts. About 0.5 gram of a mixture of sodium chloride and iodide is dissolved in 40—50 c.c. of water, and 50 c.c. of 20 per cent. ammonium sulphate solution and 30 c.c. of alcohol added. An excess of 4 per cent. thallium sulphate solution is then introduced, and the mixture allowed to remain in the cold for 12 hours; the precipitated thallium iodide is then collected on a tared filter, washed with a 5 per cent. solution of ammonium sulphate in 30 per cent. alcohol, and finally with 30—50 per cent. alcohol, and, after drying at 100°, weighed. The alcohol is evaporated from the filtrate, and the residue made up to 300 c.c. with water; 10 c.c. of concentrated nitric acid, and the necessary quantity of silver nitrate are then added to the boiling liquid, and the silver chloride collected and weighed as usual. It does not seem possible to separate chlorine and bromine by this method.

A. R. L.

Detection of Iodates in Iodides. By F. ROBINEAU and G. ROLLIN (*J. Pharm.* [5], **26**, 485—490).—The authors show that in presence of air and moisture all the acids, even carbonic anhydride, decompose potassium iodide, and that this salt is also decomposed when moist in presence of air and light, but is unaffected in the dark,

or when the air is replaced by carbonic anhydride or nitrogen; similar results are obtained with solutions of the salt, iodine being set free, whilst the solution becomes alkaline, according to the equation $2KI + O + H_2O = 2KHO + I_2$. The inverse reaction obtains when the moist salt or its solutions are placed in the dark. Consequently they suggest that for the detection of iodates in potassium iodide, an 8 per cent. solution of the salt should be treated with a few drops of hydrogen tartrate solution and starch paste, the immediate coloration being taken as positive evidence of their presence.

T. G. N.

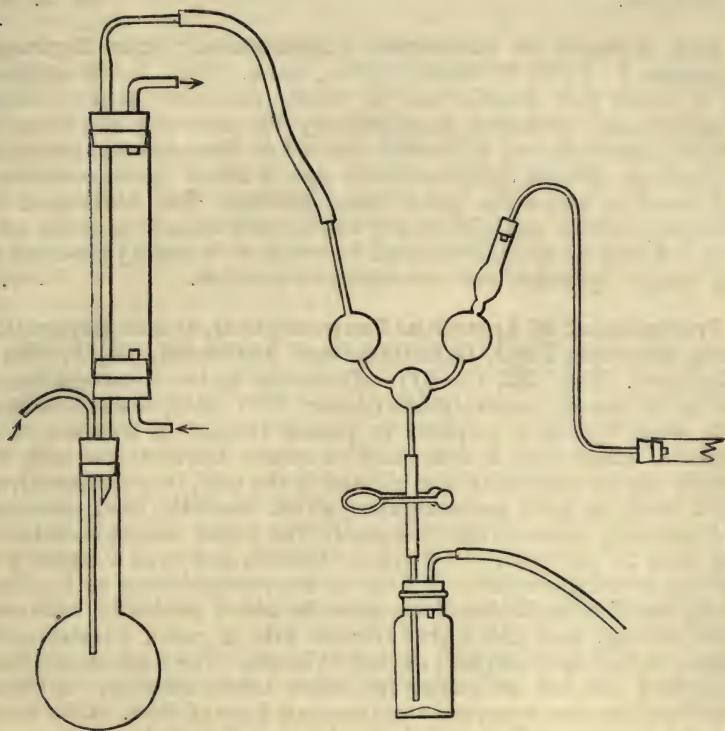
Estimation of Nitrogen in Nitrocellulose. By E. V. KEUSSLER (*Zeit. anal. Chem.*, **32**, 51—53).—The following mode of carrying out the treatment with sulphuric acid and mercury (Crum's method; see Abstr., 1887, 86) is both convenient and rapid. A Hofmann's eudiometer, with a small funnel above the stopcock, is used. The nitrocellulose (0.15 gram), wrapped in cigarette paper, is passed round the bend of the tube into the closed limb. The apparatus is then filled with mercury, and by alternately raising and lowering the level of the mercury in the pressure limb, the air is, as far as possible, removed from the cartridge. About 5 c.c. of concentrated sulphuric acid is then introduced through the funnel, and any air, disengaged by its contact with the substance, is expelled. After waiting 10 minutes for the nitrocellulose to dissolve, the tube is held so as to press the palm of the right hand against the open end, and the thumb against the stopcock, and whilst keeping the tube vertical the mercury is thrown up into the acid in the usual manner, as long as nitric oxide is evolved. The gas is measured in the same tube.

M. J. S.

Estimation of Nitrogen in Organic Nitrates. By P. RUETZOFF (*J. Russ. Chem. Soc.*, **23**, 382—388).—The apparatus used by the author to estimate the nitrogen in such substances as nitroglycerol consists of a round-bottomed flask of 150 c.c. capacity, into which are introduced about 25 grams of crystallised ferrous sulphate, 70 c.c. of hydrochloric acid of sp. gr. 1.12, and 0.3—0.5 gram of the substance to be analysed. Connected with the tube passing through the condenser is a Y-shaped bulb tube, into which an almost saturated solution of potassium carbonate can be forced up from the bottle below, so as to fill the lower bulb, and also the side bulbs to about a fourth of their volume. The wide tube sealed on to the last bulb contains solid potassium hydrogen carbonate, and is connected by means of a glass tube with a combustion tube, 40 cm. long and 12 mm. wide, containing a spiral of copper wire gauze, 25—30 cm. long. The other end of the combustion tube is attached to a Schiff's nitrogen apparatus.

Carbonic anhydride is passed into the flask and through the whole apparatus (which has previously been tested to see that it is air-tight), in order to expel the air. The level of the potassium carbonate solution should at this period just reach the lower bulb, so that the apparatus may not become choked up by the deposition of crystals of

potassium hydrogen carbonate. When the air has been completely driven out, the tube containing the copper is heated in a combustion furnace, and the solution of potassium carbonate introduced into the bulbs. The flask is now heated and occasionally shaken, so that a regular stream of gas comes off. The gas is nitric oxide mixed with the vapour of water and hydrochloric acid, the last two being absorbed by



the solution in the bulb tube and by the dry potassium hydrogen carbonate. After three-quarters of an hour, the black, opaque solution in the flask has become reddish-brown and transparent, and very little gas rises in the nitrogen apparatus. The boiling is continued for 10–15 minutes longer, after which the flame is lowered, and carbonic anhydride passed for about half an hour, to sweep out the last traces of gas. The nitrogen apparatus is then disconnected, and the volume read off after cooling.

The results obtained by the author are good: for example, the percentage amount of nitrogen found in trinitroglycerol was 18.36, 18.55, and 18.48; the calculated being 18.50. J. W.

A Source of Error in the Estimation of Phosphoric acid by Magnesia Mixture. By N. v. LORENZ (*Zeit. anal. Chem.*, 32, 64–67)
—In the absence of citric acid, the simultaneous precipitation of some

magnesia (about 1 per cent.) cannot be prevented, even by adding the magnesia mixture drop by drop. When 2 per cent. of citric acid (in the form of the usual ammonium citrate solution) is added, and then the magnesia mixture, drop by drop, not a trace of magnesia can be found in the precipitate, and, with larger proportions of the citrate solution, the slow addition of the magnesia mixture is quite superfluous.

M. J. S.

Can Arsenic be converted quantitatively into Hydrogen Arsenide? By F. W. SCHMIDT (*Zeit. anorg. Chem.*, **1**, 353—359).—It is found that arsenic can be wholly converted into hydrogen arsenide and estimated quantitatively by absorbing the latter in silver nitrate solution, if, towards the end of the operation, a solution of stannous chloride in hydrochloric acid is added to the contents of the vessel in which the gas is being evolved. The addition of the stannous chloride precipitates any arsenic still remaining in the solution in a very finely divided state, in which it is readily attacked by the nascent hydrogen and converted into arsenide.

H. C.

Precipitation of Arsenic as Pentasulphide, and its Separation from Bismuth, Lead, Cadmium, and Antimony. By F. NEHER (*Zeit. anal. Chem.*, **32**, 45—51).—Following up the investigations of McCay on arsenic pentasulphide (*Abstr.*, 1887, 213), the author finds that when hydrogen sulphide is passed through a solution of an arsenate mixed with a sufficiency of strong hydrochloric acid, the arsenic can be completely precipitated in the cold, in a comparatively short time, as pure pentasulphide, whilst bismuth, lead, cadmium, and antimony remain unprecipitated. The liquid should contain not less than 29 per cent. of hydrogen chloride, and even a higher percentage seems favourable. All rise of temperature must be avoided; the hydrochloric acid should therefore be added gradually, with artificial cooling, and the liquid treated with a rapid, uninterrupted stream of hydrogen sulphide during $1\frac{1}{2}$ hours. The flask should then be corked and left for one or two hours before filtering. A Gooch crucible is the most convenient and accurate form of filter. After washing the precipitate, first with hydrochloric acid and then with water, until free from acid, a trace of free sulphur should be removed by repeated washings with hot alcohol. The precipitate is dried at 100° until constant; it is anhydrous. The reported test analyses, with quantities varying from 0.1 to 0.3 gram, show no error greater than 0.3 milligram.

M. J. S.

Methods of Estimating the Sulphur in Sulphides. By L. P. MARCHLEWSKI (*Zeit. anal. Chem.*, **32**, 1—45).—The sulphur may either be oxidised to sulphuric acid, or estimated by a direct method. Oxidation by aqua regia, by potassium chlorate and hydrochloric or nitric acid, or by fuming nitric acid alone, gives good results; so also do oxidation with permanganate, and the dry method of Fresenius, both of which, however, occupy much time. Oxidation by chlorine or bromine in alkaline solution, or by hydrogen peroxide, is incomplete. If the sulphuric acid formed is estimated volumetrically, a

saving of time over the gravimetric method can be effected. The alkalimetric methods of Baumann, Clemm, Wilsing, Gawalovski, Knöfler, and Bohlig are of insufficient accuracy; Andrews' method (Abstr., 1890, 414), on the contrary, is exact and rapid.

If the sulphur is expelled, in the form of hydrogen sulphide, by hydrochloric acid, it may be accurately estimated by passing it through ammoniacal hydrogen peroxide, which oxidises it to sulphate, or through standard iodine. Concentrated nitric acid does not oxidise hydrogen sulphide completely unless warmed to 80° ; aqua regia is more energetic, but the use of either entails complications. Permanganate may be used, but, unless the manganese is removed before precipitating the sulphuric acid, the results are too high. De Koninck's second method (Abstr., 1889, 437) is both convenient and accurate. Weil's method with alkaline copper solution is not trustworthy. Von Berg's process (Abstr., 1887, 301) gives good results. The colorimetric methods of Osmond (with silver nitrate), and Hardy and Arnold (with lead acetate), are of service in some cases, such as the analysis of irons, but the passage of the gas through the absorbing vessels must be extremely slow.

M. J. S.

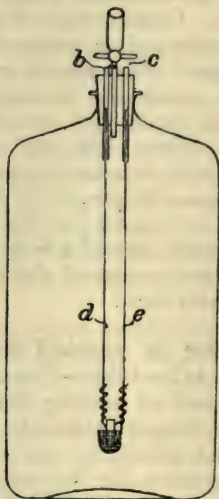
Estimation of Sulphur in roasted Pyrites. By G. LUNGE (*Zeit. angew. Chem.*, 1892, 447—449).—The author has long ago concluded that Watson's method of heating the burnt pyrites with a known weight of sodium hydrogen carbonate, and afterwards titrating the excess of undecomposed alkali, is one of the quickest, simplest, and most trustworthy processes for the estimation of the sulphur. But, in order to get accurate results, the following details must be adhered to:—The mixture must be heated for 10 minutes at a temperature just high enough to convert the acid carbonate into the normal salt. The crucible must now be covered, and then heated strongly for 15 minutes, but the temperature must not be high enough to fuse the mass. On no account should the mixture be stirred during the ignition. The mass when treated with boiling water often refuses to give a clear filtrate, but this inconvenience may be avoided by adding some strong brine.

L. DE K.

Estimation of Sulphur in Coals and Organic Substances. By W. HEMPEL (*Zeit. angew. Chem.*, 1892, 393—394).—Berthelot having successfully estimated organic sulphur by simply burning the substance in a shell containing oxygen, the author has repeated the process, but with a much simpler apparatus. The substance to be analysed is pressed into a little platinum wire cylinder to which a longish platinum wire is attached.

The combustion is effected in an ordinary glass bottle of about 10 litres capacity (see illustration), which is fitted with a trebly perforated india-rubber stopper. Through this passes a tube with a glass stopcock, the outer end of which widens into a cylinder of about 50 c.c. capacity; also two glass tubes, to the lower ends of which are fused two long, 0.6 mm. thick, platinum wires. One of these wires carries at its lower end a little platinum basket made by folding a piece of platinum wire gauze. When lowered, this basket should be

at a distance of about 25 cm. from the bottom of the flask. For the purpose of electric firing, a little mercury is poured into the tubes *b* and *c*, so as to establish a sure contact with the wires of a 6-cell battery. To carry on an experiment, the india-rubber stopper is removed from the flask, the cylinder containing the substance is put into the basket, and its wire is twisted round the wires *d* and *e* in



such a manner that the electric current is obliged to pass through it. The flask is now filled with distilled water, closed with an ordinary stopper, and placed, inverted, in a porcelain dish containing a little water. After removing the stopper, the flask is filled with oxygen, most conveniently delivered from a cylinder containing the compressed gas. When the flask is filled, the stopper is again put in, the flask is removed from the dish, and put into its normal position. After carefully removing the stopper, the rubber stopper, with its fittings, is inserted. As oxygen is somewhat heavier than air, there is but very little loss of this gas during the operation. The rubber stopper is now firmly tied down with wire, and the substance fired.

After cooling, a mixture of 100 c.c. of water, 5 c.c. of hydrochloric acid, and a little drop of bromine is introduced into the flask by means of the stopcock. After standing for about an hour, or at all events until there is no longer any cloudy appearance, the contents of the flask are washed into a beaker, filtered if necessary, and precipitated with barium chloride. The test analyses are very satisfactory.

L. DE K.

Volumetric Estimation of Sulphuric acid in Sulphates. By E. STOLLE (*Zeit. angew. Chem.*, 1892, 234—235).—The process proposed by the author is based on the following reactions:—Barium chromate dissolves in hydrochloric acid, with formation of barium

chloride and barium dichromate, and from this solution the barium chromate is completely reprecipitated on adding ammonia. If, now, the solution of a sulphate is mixed with a hydrochloric acid solution of barium chromate, the whole of the sulphuric acid is thrown down as barium sulphate. If the liquid is now neutralised with ammonia, the remaining barium is precipitated as chromate, and the chromic acid still remaining in solution therefore serves as a measure of the amount of the sulphuric acid. The actual process is as follows:—A weighed quantity of the substance is dissolved in a 500 c.c. flask, and the solution of barium chromate is added, best from a burette, until the sulphuric acid seems completely precipitated. After adding a slight excess of ammonia, the whole is made up to the mark, filtered, and the chromic acid estimated in an aliquot part of the liquid by means of ferrous sulphate in the usual manner. The test analyses are very satisfactory. L. DE K.

Estimation of Sulphurous Acid in Wine. By M. RIPPER (*J. pr. Chem.* [2], 46, 428—473).—As a standard method for the estimation of sulphurous acid in wines, the author employs that proposed by Haas (Abstr., 1882, 773), care being taken that the traces of hydrogen sulphide and oxygen, with which carbonic anhydride made from marble and hydrochloric acid are contaminated (compare Pfordten, Abstr., 1885, 836), are removed by washing with potassium permanganate and chromous chloride, and that the ignited barium sulphate (in which form the sulphurous acid is finally weighed) is freed from barium sulphide and chloride by successive treatment with bromine water and hydrochloric acid. This method is far too lengthy for general use as an analytical process, and may be successfully substituted by the following:—50 c.c. of the wine is pipetted into a distillation apparatus full of hydrogen, and 5 c.c. of sulphuric acid (1 : 3) is added; the flask is heated in a glycerol bath at 80—85° for three-quarters of an hour, a current of hydrogen being passed through the apparatus. The evolved sulphurous anhydride is absorbed in a flask containing 20 c.c. of normal potassium hydroxide, through which the hydrogen bubbles, and which, after the time stated, is acidified with 10 c.c. of sulphuric acid (1 : 3), and titrated with *N*/50 iodine solution, starch being used as an indicator.

As a still more rapid method, the author recommends direct titration of the wine with iodine solution; this is only applicable to white wines, or to those whose colour after dilution is sufficiently pale to admit of the recognition of the iodine starch blue; red wines must be treated by the distillation method, if it be necessary to make a determination of the sulphurous anhydride in them; but, inasmuch as their colour does not admit of their being sulphured, this is seldom necessary.

While this method was being investigated, it was noted that the sulphurous anhydride in wine does not exist entirely, or even chiefly, in the form of sulphurous acid or alkaline sulphites, as heretofore supposed; after numerous experiments, detailed in the paper, the conclusion was drawn that the wine contains aldehyde sulphite (compare Boessneck, Abstr., 1888, 942). By direct titration of the wine,

it is possible to determine the "free" sulphurous acid (that existing as sulphurous acid and sulphites) and the "total" sulphurous acid, the difference between the two being the "aldehyde" sulphurous acid.

50 c.c. of wine from the freshly opened bottle is pipetted into a 100 c.c. flask, which has been swept out with carbonic anhydride; 5 c.c. of dilute sulphuric acid (1 : 3), and some starch solution are added, and *N*/50 iodine solution is run in with continual shaking, until the blue colour is permanent for some little time. The end reaction is very distinct, but after some minutes the tannin, &c., in the wine will begin to absorb iodine, and the colour will be again bleached. This titration serves for the estimation of the "free" sulphurous acid. Inasmuch as the "aldehyde" sulphurous acid is not oxidised, at all events for some time, by iodine in presence of sulphuric acid, it must be decomposed by alkali before the total sulphurous acid can be determined. For this purpose, 50 c.c. of the wine is pipetted into a 200 c.c. flask, containing 25 c.c. of normal potash solution, care being taken that the nose of the pipette is beneath the surface of the liquid. After 10—15 minutes, 10 c.c. of sulphuric acid (1 : 3) and some starch are added, and titration with *N*/50 iodine solution effected as before.

Some experiments are quoted to show that the "free" sulphurous acid in wine slowly becomes converted into "aldehyde" sulphurous acid, and that the total sulphurous acid decreases with the age of the wine. A. G. B.

Estimation of Potassium as Perchlorate. By W. WENSE (*Zeit. angew. Chem.*, 1892, 233—234).—The author (compare this vol., ii, 46) has proved that by adding a small quantity of perchloric acid to alcohol, the potassium perchlorate becomes practically insoluble therein, and may be very accurately estimated in this manner.

If, when estimating potassium in carnallite, the operator wishes to obviate the removal of sulphates, the following modification of the process is recommended:—The solution is evaporated with perchloric acid to decompose the chlorides, the residue is extracted with acid alcohol, and finally dissolved in hot water. This solution is evaporated in a platinum dish, the residue calcined to convert the perchlorate into chloride, then dissolved in water, and titrated with a standard solution of silver nitrate. L. DE K.

Analysis of Hydrogen Alkali Carbonates. By VIZERN (*J. Pharm.* [5], 26, 385; compare Abstr., 1892, 1130).—The total alkali present is first determined by normal sulphuric acid solution; another portion of the salt is converted into normal carbonate by the addition of an alcoholic solution of an alkali hydroxide, and the resulting solution is divided; in the one half, the alkali present is determined by normal sulphuric acid directly, and in the other, after decomposition of the carbonate by means of barium chloride solution. From the results, a formula can easily be deduced to determine the normal carbonate present as an impurity. T. G. N.

Estimation of Soda in Soap. By W. H. Low (*J. Anal. Chem.*, **6**, 423—431).—A few grams of soap is treated with 50—100 c.c. of neutral alcohol, heated to boiling, and standard hydrochloric acid, in excess of the quantity necessary for the decomposition of the carbonate, run in; the carbonic anhydride is expelled by strong ebullition, phenolphthaleïn added, and the liquid titrated with standard soda. The soda unites with the fatty acids, and a neutral soap solution is obtained. The difference between the hydrochloric acid taken and the acid equivalent of the alkali employed gives the amount of sodium carbonate. Blue lacmoid solution is added, and the liquid titrated with standard hydrochloric acid. As the colour changes to reddish before all the combined alkali is neutralised by the hydrochloric acid, the addition of the acid must be continued until a pure, bright red coloration is obtained which is not altered by the further addition of another drop of acid. The end reaction is quite distinct, even with dark-coloured soaps, but with these the indicator must be freely used.

To determine the amount of the fatty acids, where the molecular weight is not known, the solution is again made alkaline, evaporated to dryness, taken up with water, and the fatty acids separated by the addition of excess of hydrochloric acid; the mixture is then cooled, the separated acids collected, washed with water, and the water removed mechanically as far as possible; the acids are now washed into a flask with hot alcohol, and titrated with alcoholic soda free from carbonate, phenolphthaleïn being used as indicator; finally the solution is evaporated to dryness and the residue weighed. The difference between the weight and that of the soda employed gives the amount of the fatty anhydrides more accurately than the direct weighing of the fatty acids, as in the latter case loss and anhydride formation occur during the drying. If soluble fatty acids are present, the filtrate from the insoluble fatty acids is shaken with ether, the ethereal extract mixed with alcohol, neutralised with alcoholic soda, using phenolphthaleïn as indicator, evaporated to dryness, and the residue weighed.

A. J. G.

Electrolysis of Metallic Formates. By H. S. WARWICK (*Zeit. anorg. Chem.*, **1**, 285—312).—After giving details of the electrolysis of certain formates, the author sums up his results as follows:—The weight of copper, cadmium, or zinc precipitated in a given time is proportional to the strength of the salt solution; the presence of a moderate amount of free acid exerts no essential influence on the result. By augmenting the distance between the poles, the quantity of metal precipitated is decreased, although the diminution becomes less as the distance between the electrodes increases. Rise of temperature causes an increase in the quantity of metal precipitated, the maximum amount being obtained at 80° with neutral and acid solutions of the copper salts, and at 60° with acid solutions of the cadmium salt. The amount of zinc precipitated in solutions containing free acid decreases, however, with the rise of temperature. Attempts to produce compact coherent deposits of cadmium and zinc in neutral solutions of their formates were unsuccessful; copper and cadmium

are, however, completely precipitated in acid solution, as is also zinc, but the precipitated metal is, in the last case, spongy. Lead separates, chiefly at the cathode, both from acid and neutral solutions; manganese is precipitated at both poles, but the quantity of peroxide which separates at the cathode is, on addition of free acid, reduced to mere traces. The following separations may be satisfactorily effected:—Copper from zinc, cobalt from nickel, and cadmium from zinc and manganese. It was found impossible to precipitate copper in the presence of iron or cadmium, as also zinc in the presence of iron, cobalt, or nickel; it also seems impossible to estimate cadmium in the presence of iron, nickel, or cobalt.

A. R. L.

Separation of the Metals precipitated by Hydrogen Sulphide in Acid Solutions. By U. ANTONY and L. NICCOLI (*Gazzetta*, 22, ii, 408—417).—The metals precipitated by hydrogen sulphide from acid solutions may be divided into three sub-groups, as follows:—1. Antimony, tin, bismuth, cadmium, and lead, whose sulphides are soluble in hydrochloric acid. 2. Arsenic and copper, whose sulphides, although insoluble in hydrochloric acid, are dissolved by nitric acid. 3. Mercury, platinum, and gold, the sulphides of which are not decomposed by either hydrochloric or nitric acid. This classification forms the basis of a scheme which possesses many advantages over other methods employed for separating the above metals.

The precipitate obtained with hydrogen sulphide in the acid solution is washed until the washings are no longer acid, then treated with hydrochloric acid (sp. gr. 1.1), boiled, and the liquid decanted through a filter; the residue is again boiled with hydrochloric acid, first adding a little hydrogen sulphide solution, and is finally decanted through a second filter, the filtrates being then united. During the above treatment, contact with the air is to be avoided, as copper sulphide readily oxidises and dissolves. The residue insoluble in hydrochloric acid is washed on a filter, first with cold, then with hot, water, until the filtrate gives no precipitate with silver nitrate; any lead chloride formed is precipitated as chromate from the hot water washings.

The residue on the filter is then twice boiled with nitric acid (sp. gr. 1.2), decanting the liquid through a filter and uniting the filtrates. The insoluble residue is washed on a filter, when any silver chloride formed by the action of hydrochloric acid on the sulphide can be detected by dissolving it in ammonia; the residue is finally washed well, and dried at 100°.

The hydrochloric acid solution is evaporated to dryness on the water-bath, the residue moistened with ammonia solution, stirred with yellow ammonium sulphide solution, and heated below the boiling point for a short time. On filtering the cooled solution, the antimony and tin are contained in the filtrate, whilst bismuth, cadmium, and lead sulphides remain undissolved. If both cadmium and antimony are present, cadmium sulphantimonate may be formed, but as this decomposes on heating, the residue should be boiled with ammonium sulphide, filtered, and the two filtrates united; the presence of antimony in the solution is betrayed by the characteristic orange-red colour

of its sulphide, obtained on evaporating a little of the solution to dryness on the water-bath. As, however, the colour may be masked by that of free sulphur or stannic sulphide, the residue is dissolved by warming with a few drops of hydrochloric acid on platinum foil; the characteristic black stain due to reduced antimony is then obtained on adding a fragment of zinc. The remainder of the filtrate is now acidified with hydrochloric acid, warmed, the solution decanted, and the precipitate dissolved by boiling with concentrated hydrochloric acid; the solution is then boiled with metallic antimony to convert the tin into stannous chloride. On cooling, filtering, and adding a few drops of saturated mercuric chloride solution, mercurous chloride separates if the solution contains more than 0.01 per cent. of tin.

The residue insoluble in ammonium sulphide may contain bismuth, lead, and cadmium; it is dissolved in the minimum quantity of nitric acid, the solution filtered, excess of ammonia added, and again filtered. Cadmium is precipitated from the filtrate by hydrogen sulphide; the residue is washed, boiled with sulphuric acid (sp. gr. 1.11), and the solution filtered. The filtrate contains the bismuth, which gives the hydrate on adding ammonia, and black bismuthous oxide on pouring into alkaline potassium stannite solution. The residue undissolved by sulphuric acid is lead sulphate, and is identified in the usual way.

The nitric acid extract of the mixed sulphides may contain arsenic and copper, the detection of which presents no difficulties.

The dried residue insoluble in nitric and hydrochloric acids may contain mercury, platinum, and gold; it is heated in the Bunsen flame, in a narrow glass tube closed with cotton wool. Mercuric sulphide sublimes, giving the characteristic black ring, which is readily distinguished from the more volatile sublimate of sulphur due to the decomposition of platinic or auric sulphide. The residue which resists sublimation is removed and heated strongly, to obtain the metals, which are then dissolved in chlorine water or nitrohydrochloric acid, and the solution evaporated to dryness on the water-bath; the aqueous solution of the residue is boiled with oxalic acid, when the gold is deposited as such. The platinum remains in solution, and may be separated as ammonium platinumchloride if the usual precautions are taken.

W. J. P.

New Method for the Titration of Ferric Salts. By H. MORAHT (*Zeit. anorg. Chem.*, 1, 211—216).—This method consists in titrating a solution of a ferric salt with a standard solution of potassium ferrocyanide, employing potassium thiocyanate as indicator, and therefore obviously depends on the constancy of composition of the precipitate—Prussian blue. This has, however, been satisfactorily settled by Classen (*Mohr's Titriermethode*, 6 Aufl., 235; see also Reynolds, *Trans.*, 1887, 644). The solution, in which all the iron must be present as ferric salt (if it be not, it is oxidised, as described below, with potassium chlorate), is introduced into a stoppered flask of 500 c.c. capacity, together with some potassium thiocyanate and about 50 c.c. of ether, when the latter immediately assumes the well-known, deep red colour of ferric thiocyanate. A

standard solution of potassium ferrocyanide is now run in by degrees from a burette, shaking briskly at intervals, until the ethereal layer is colourless, or of a faint rose tint. This test is to be regarded as preliminary. A second is now made as before, but a volume of ferrocyanide solution, a little less than that found in the previous experiment, is added at once to the ferric salt, and, after shaking the mixture, potassium thiocyanate and a sufficient quantity of ether are introduced. On again shaking and allowing to remain, the ethereal layer will be of a faint rose tint; it is decolorised by the further addition of ferrocyanide solution. As the surface of the Prussian blue is slightly violet, the disappearance of colour from the ethereal layer is best observed by looking through it obliquely from below. The ferrocyanide solution may be standardised with potassium permanganate solution, but the final point is difficult to determine exactly. It is therefore preferable in standardising the ferrocyanide solution to employ a weighed quantity of pure iron, which is dissolved in hydrochloric acid with the addition of potassium chlorate, and after boiling off the excess of chlorine, the test is continued as already described. The titration may be performed either in neutral or acid solutions. The test analyses were satisfactory.

A. R. L.

Volumetric Estimation of Cobalt. By W. J. KARSLAKE (*J. Anal. Chem.*, 6, 469—470).—The cobalt is precipitated as potassium cobaltinitrite, the precipitate boiled with aqueous potash until the liquid becomes colourless, filtered, the filtrate treated with permanganate solution until a violet coloration is produced, then slightly supersaturated with sulphuric acid, and an excess of permanganate solution added: it is then strongly acidified, heated to 80° , and the excess of permanganate titrated back with oxalic acid. The amount of cobalt is deduced from the permanganate required to convert the nitrous acid of the salt $K_3Co(NO_2)_6$ into nitric acid.

A. J. G.

Volumetric Estimation of Chromium. By A. PERRAULT (*Chem. Centr.*, 1892, ii, 807—808; from *Mon. Sci.* [4], 6, 722—723).—A modification of Carnot's hydrogen peroxide method (Abstr., 1889, 311, 443). Commercial hydrogen peroxide, diluted with 10 times its volume of water, is employed, and its strength determined on each occasion of using as follows:—3 c.c. of a solution of potassium dichromate containing 37 grams per litre is diluted to a litre, 50 c.c. of this ($= 0.003774$ gram of CrO_3) is neutralised with 10 per cent. ammonia, and 1.5 c.c. of 10 per cent. solution of hydrochloric acid added; to this the hydrogen peroxide solution is added, drop by drop, until further addition causes no blue coloration.

In estimating chromium in the chromic compounds, a dilute solution of the chromium compound is prepared, and $\frac{1}{2}$ litre of the solution heated at 100° ; hydrogen peroxide is run in until the grey coloration first produced has completely vanished, ammonia is then added, and the mixture heated for 10 minutes, when the colour, originally green, becomes brown, and finally clear yellow, the solution then containing ammonium chromate. After cooling, it is made up to 500 c.c., and 50 c.c. titrated as above described.

If both chromates and chromic compounds are present, the latter are converted into chromic acid, and the total chromium estimated in one portion, whilst in a second portion the preformed chromic acid is estimated, and the chromic compounds found from the difference between the two titrations.

A. J. G.

New Method of estimating Vanadic Oxide. By A. ROSENHEIM and C. FRIEDHEIM (*Zeit. anorg. Chem.*, 1, 313—317).—The method depends on the gravimetric estimation of the carbonic anhydride which is evolved in accordance with the equation $V_2O_5 + H_2C_2O_4 = V_2O_4 + H_2O + CO_2$, when a solution of vanadic acid is boiled with one of oxalic acid in the presence of sulphuric acid. The results are not affected by the presence of phosphoric, tungstic, or molybdic acid, and the method has an advantage over that of Holverschedt (*Abstr.*, 1890, 1343), in that the base may be estimated in the same portion. For this purpose, the residual solution, after expelling the carbonic anhydride, is evaporated to a syrupy consistence in order to decompose the excess of oxalic acid, oxidised with nitric acid, neutralised with ammonia, and, after removing the acids with mercurous nitrate, the base is determined in the filtrate.

A. R. L.

Palladium Compounds. By M. FRENKEL (*Zeit. anorg. Chem.*, 1, 217—239).—Attempts to prepare hydrogen palladious cyanide by extracting an acidified solution of potassium palladious cyanide with ether were unsuccessful. Potassium palladious cyanide is decomposed on boiling a solution of it with hydrochloric acid. The whole of the palladium is in fact precipitated as palladious cyanide without the use of mercuric cyanide (Fresenius) when potassium cyanide is added to a solution of palladious chloride, and after acidifying the mixture with hydrochloric acid, the hydrogen cyanide is driven off by boiling. The precipitation of silver chloride on adding silver nitrate to solutions of the chlorides of palladium is incomplete, and the precipitate is contaminated with palladium compounds. Accurate results are obtained, however, both in the determination of the metal and halogen, by heating the palladium chloride solution with alcoholic sodium hydroxide on the water bath, collecting, washing, drying, and weighing the precipitated metallic palladium; the chlorine is then estimated in the filtrate as silver chloride after acidifying with nitric acid.

When potassium chromate is added in excess to a solution of palladious chloride, the palladium is quantitatively precipitated as a reddish-brown precipitate, which when heated at 110° has the composition $15PdO, PdCl_2 + 11H_2O$. The latter reaction can be made use of for the estimation of palladium, as the new compound yields metallic palladium on ignition; it may, perhaps, also serve for the separation of palladium from other metals of the platinum group. Palladosoammonium chloride, $PdCl_2 \cdot 2NH_3$, is precipitated when a solution of ammonium palladious chloride is boiled with potassium chromate.

A. R. L.

Estimation of Iron in Spring Water. By F. GERHARD (*Arch. Pharm.*, 230, 705—710).—The use of tannin (from galls) as a colorimetric reagent is proposed; by its means $\frac{1}{15}$ milligram of iron per litre can be detected. The following solutions are made up; (1) 1 part of crystallised sodium pyrophosphate in 20 parts of water; (2) 1 part of tannin in 20 parts of dilute alcohol; (3) 0.898 gram of iron-alum, and 2.5 grams of crystallised sodium pyrophosphate in 1 litre of water; this contains 0.1 milligram of iron per c.c.

If the water is fresh and still clear, 100 c.c. of it is taken, 20 c.c. of (1) and 5 drops of (2) are added, and the colour is compared with that obtained with a mixture of 100 c.c. of water free from iron with 20 c.c. of (1), 5 drops of (2), and a certain quantity, best 1 c.c., of (3). If the water to be examined already contains a precipitate, it is shaken up, and 150 c.c. are placed in a flask and heated with 1 gram of oxalic acid. To the hot liquid a granule of potassium citrate is added (to prevent precipitation of iron), the solution is saturated with calcium carbonate to remove the oxalic acid, filtered, and treated as above with 20 c.c. of (1) and 5 drops of (2). In this case, the results are not quite so accurate.

C. F. B.

Impurities in Crude Methyl Alcohol. By E. BAREILLOT (*Compt. rend.*, 115, 1315—1317).—When 20 c.c. of chloroform is agitated with a mixture of 10 c.c. of methyl alcohol, 15 c.c. of a solution of sodium hydrogen sulphite of sp. gr. 1.325, and 5 c.c. of water, the coefficient of division between the two non-miscible liquids is such that the chloroform retains its original volume when the methyl alcohol contains no impurity other than acetone. If, on the other hand, the alcohol contains impurities such as benzene, diallyl, &c., the chloroform increases in volume in proportion to the quantity of impurity.

In actual work, the methyl alcohol, sulphite solution, and water are first thoroughly mixed in the proportions given, and the mixture is then agitated with the 20 c.c. of chloroform in a graduated tube, the increase in the volume of the chloroform being read off. The increase in volume in c.c. multiplied by 10 gives the percentage of impurity other than acetone.

At least 10 per cent. of impurities other than acetone must be present if the alcohol is to be effective as a methylator, but many commercial samples of methyl alcohol contain only from 2 to 5 per cent. of such impurities.

C. H. B.

Analysis of Explosive Nitro-compounds. By P. G. SANFORD (*J. Anal. Chem.*, 6, 311—318).—In analysing dynamites, the water is estimated directly by exposure for 6—8 days over calcium chloride and the kieselguhr by extracting the nitroglycerol with ether and weighing the residue; the nitroglycerol being calculated from the difference. Blasting gelatins, after estimation of the water as above, are treated with a mixture of ether and alcohol, and the insoluble residue, consisting of wood-meal, nitre or other salts, is collected, dried, and weighed. From the solution, the nitrocellulose is precipitated by the addition of chloroform, collected on a linen filter, redissolved in a mixture of ether and alcohol, reprecipitated, collected, partly dried at 40°, and scraped

off the linen filter; it is then again dried at 40° until constant, and weighed. The nitroglycerol is best estimated by difference, but may be obtained directly by evaporating the filtrate from the nitrocellulose at 30—40° and weighing the residue. In analysing guncotton, the water must be estimated immediately on opening the sample, by drying at 100°; the dried residue is then exposed to the air for two hours, treated with ether-alcohol to remove the soluble pyroxylin, and the insoluble residue, consisting of unchanged cotton and the hexanitate, collected on a linen filter, dried at 100°, and weighed. The weight of the unchanged (non-nitrated) cotton is obtained by twice boiling a fresh sample with sodium sulphide solution and weighing the insoluble residue. The best test for the purity of guncotton is, however, the determination of the nitrogen, which is best effected by Crum's method, using a Lunge's nitrometer.

A. J. G.

Estimation of the Volatile Fatty Acids in Butter Fat. By A. PARTHEIL (*Chem. Centr.*, 1892, ii, 635—636; from *Apoth. Zeit.*, 7, 435).—5 grams of filtered, dry butter fat is placed in a flask of 300—350 c.c. capacity and 2 c.c. of 50 per cent. aqueous soda and 20 c.c. of glycerol added. The mixture is then carefully boiled over wire gauze until all the water is expelled, the flask being gently rotated the while; the heating is then continued with a smaller flame. After 15—20 minutes, a clear soap solution is obtained, which, after cooling, is mixed with 90 c.c. of water and 50 c.c. of dilute sulphuric acid (50 c.c. of pure acid per litre), some fragments of pumice added, and the mixture distilled until 110 c.c. has passed over. The author regards the method as quicker and more convenient than the older methods, but the test analyses appear to be far from satisfactory.

A. J. G.

Baudouin's Test for Sesame Oil. By V. VILLAVECCHIA and G. FABRIS (*Zeit. angew. Chem.*, 1892, 509—510).—The authors have made a thorough investigation of this test, and propose to apply it as follows:—

0.1 gram of sugar is dissolved in a test tube in 10 c.c. of hydrochloric acid, sp. gr. 1.19. 20 c.c. of the sample of olive oil is then added, the whole thoroughly shaken for a minute, and allowed to settle. If the oil is pure, the acid and oily layers retain their original colour, but if sesame oil is present they are *both* of a decidedly reddish shade.

L. DE K.

Estimation of Fat in Bread. By M. WEIBULL (*Zeit. angew. Chem.*, 1892, 450—451).—The author was surprised to find in a sample of bread much less fat than might have been expected considering the nature of the flour used. Prolonged treatment (160 hours) in the Soxhlet tube gave a reasonable percentage of extract, but this was afterwards found to consist mainly of glucose. Fairly accurate results can, however, be obtained as follows:—About 2 grams of the sample is boiled for at least an hour with 30 c.c. of water acidified with sulphuric acid; when the starchy matter has dissolved, the liquid is neutralised with powdered marble, and the mixture is soaked up in blotting paper of the kind employed in Adams' milk

process. After thoroughly drying, the paper is put into a suitable extraction apparatus and extracted with anhydrous ether for about eight hours.

L. DE K.

Analysis of Bees-wax by Hübl's Method. By J. A. ANTUSHEVITCH (*J. Russ. Chem. Soc.*, **23**, 223—235).—The author has analysed a large number of waxes both pure and commercial, according to Hübl's method. He finds that heating on a water-bath for three-quarters of an hour with alcoholic potash, as Hübl recommends, is not sufficient to effect the complete saponification of the myristyl palmitates. He heats for four hours over a free flame. The normal ratio of the quantity of potash necessary for saponification to that necessary for neutralisation of the free acid present he fixes at 3.75. The following formula is given for finding the quantity of stearic acid present in wax candles:—

$$x = \frac{284(S - A/3.75)}{56.1};$$

x is the percentage of stearic acid, S the number of milligrams of potash necessary for the neutralisation of 1 gram of substance, and A the number necessary for saponification of the same quantity.

J. W.

Estimation of Water and of Free Fatty Matter in Soap. By J. A. WILSON (*Chem. News*, **66**, 200).—2.5 grams of the soap, melted in a porcelain dish, and heated on a water-bath with 5 c.c. of absolute alcohol until dissolved, is mixed with 10 grams of ignited sand, and, after exposure on the water-bath for an hour, is treated again with 5 c.c. absolute alcohol; it is then heated to constant weight in an air-oven at 100—105°, which may take from three to six hours, according to the quantity of water in the soap. Moreover, provided the soap does not contain free alkali, the residue may be extracted in a Soxhlet apparatus for fat estimation.

D. A. L.

Estimation of Theobromine in Cacao Beans. By P. Süss (*Zeit. anal. Chem.*, **32**, 57—63).—The methods of Tuchen, Bell, König, Zipperer, Wolfram, Trojanowski, and Diesing yield widely varying results. In contradiction to Diesing, the author finds that the cacao fat may be extracted by light petroleum without dissolving a trace of theobromine. Diesing extracts the theobromine by chloroform in a Soxhlet's extractor, but the following method gives a much higher yield and seemingly a purer product. The fermented bean is intimately mixed with an equal weight of purified quartz sand, and 6 grams of this mixture is extracted for 10 hours with light petroleum. The residue is boiled for half an hour with 200 c.c. of water and 6 grams of elutriated lead oxide, decolorised, and filtered, the residue being twice more boiled with 100 c.c. of water. The filtrates are evaporated to 10 c.c., introduced into a separator bulb, and shaken for three minutes with 100 c.c. of chloroform, the chloroform solution being run off when perfectly clear (three hours), and the operation repeated twice more. The greater part of the chloroform is distilled off, and the remainder evaporated in a tared beaker, drying the

residue at 100°. From appearance, qualitative tests, ash, and nitrogen estimations, the product seemed to be practically pure theobromine. The yield was nearly double that obtained by Zipperer's method, and 40 per cent. higher than Diesing's, although Diesing's product was brown.

M. J. S.

Volumetric Estimation of Alkaloids. By E. LÉGER (*Compt. rend.*, 115, 732).—Referring to the paper by Barthe on the claim for priority made by Harsten (*Compt. rend.*, 1892), the author points out that in 1885 (*J. Phys. Chim.*, 11, 425) he stated that alkaloids were neutral to phenolphthalein, and that this fact could be utilised in the volumetric analyses of salts of the alkaloids.

C. H. B.

Volumetric Estimation of Alkaloids. By P. C. PLUGGE (*Compt. rend.*, 115, 1012).—A claim for priority against Barthe (this vol., ii, 146). The author described, in 1886, a method of estimating alkaloids volumetrically, using phenolphthalein and litmus as indicators (Abstr., 1887, 621—622).

C. H. B.

Analysis of Quinine Sulphate and Estimation of Quinine in presence of other Cinchona Alkaloids. By L. BARTHE (*Compt. rend.*, 115, 1085—1088).—The author admits that Léger has the prior claim as originator of a volumetric process for the estimation of alkaloids, based on the use of phenolphthalein.

If different weights of commercial quinine sulphate are agitated with a given volume of water at 15—20°, the quantity of decinormal potassium hydroxide required for the saturation of the saturated solutions is greater the greater the quantity of quinine sulphate taken. Moreover, the progressive increase in the quantity of alkali required is in a constant ratio with the weight of quinine sulphate taken. Quantities of 1, 2, 3, 4, and 5 grams of quinine sulphate respectively were agitated frequently with 100 c.c. of water at 20°, and after an hour were filtered. The solutions required respectively 4.6, 5.3, 6.0, 6.7, and 7.4 c.c. of potash solution. The constant difference, 0.7 c.c., represents the quantity of sulphates, other than quinine, present in each gram of the sulphate taken. It is the factor which measures the impurity, and the latter may be calculated to crystallised cinchonidine sulphate (equiv. = 397); then $0.7 \times 100 \times 0.0397 = 2.779$, the percentage of cinchonidine sulphate in the sulphate employed.

The analysis of quinine sulphate can, therefore, be made in the following way:—Two quantities of 1 gram and 5 grams of the salt are each agitated with 100 c.c. of water at 20° for frequent intervals during an hour, filtered, and the filtrate titrated with decinormal potash. The difference between the quantities of alkali required by the two solutions, multiplied by the expression $100 \times 0.0397 \div 4$, gives the percentage of impurity calculated as cinchonidine sulphate.

The solubility of quinine sulphate for a given temperature between 12° and 20°, and even 25°, is sensibly different, according to the conditions under which the solubility is determined. At 12°, 1000 c.c. of water dissolve 1.482 grams of quinine sulphate when the latter is

trituated and agitated with it for about an hour; at 20°, 1000 c.c. dissolve 1.744 grams, but if the liquid is allowed to remain in contact with the excess of dissolved salt, and is frequently agitated, the temperature can be reduced to 12° without any of the salt separating from solution; that is to say, 1000 c.c. contain 1.744 grams of the salt. If, on the contrary, the liquid remains at rest whilst cooling from 20° to 12°, or to 15°, the quantity of salt remaining in solution per litre is 1.482 to 1.787 grams, and is not always the same for the same final temperature. The differences are still greater if the liquid remains at rest for 24 or 48 hours, and the solubility may then be as low as 1.133 and 1.09. The solutions thus obtained are stable *after filtration*, even at temperatures several degrees below the temperature of saturation. They cannot dissolve any more quinine sulphate at the temperature at which they were formed, or at a lower temperature, but they can dissolve 9.92 grams per litre of crystallised cinchonidine sulphate, and 12.42 grams of crystallised cinchonine sulphate.

In order to estimate quinine in cinchona bark, a chloroform solution of the alkaloids obtained by any of the ordinary methods is vigorously and repeatedly agitated with a measured excess of decinormal sulphuric acid, evaporated until the chloroform is expelled, and the excess of acid estimated by means of standard alkali and litmus. Sufficient sulphuric acid is added to the mixture to redissolve the alkaloids, which are then reprecipitated by potassium hydroxide, and dissolved in chloroform. The chloroform solution is evaporated just to dryness with the exact quantity of sulphuric acid found in the first titration to be necessary for complete neutralisation. The residue is trituated with 200 c.c. of a solution of pure quinine sulphate saturated at 20°; after two hours' digestion, the liquid is filtered. The filtrate is a saturated solution of quinine sulphate containing the sulphates of the other alkaloids. 100 c.c. is titrated with potassium hydroxide, using phenolphthaleïn as indicator. Twice the volume of alkali required, *minus* 8 c.c., gives the quantity of impurities, which can be calculated to crystallised cinchonidine sulphate. The result can be controlled by estimating the quantity of quinine sulphate left on the filter.

C. H. B.

Chromic Acid as a Reagent for Albumin and Bile Pigments in Urine. By O. ROSENBACH (*Chem. Centr.*, 1892, ii, 557; from *Deut. med. Woch.*, 1892, No. 17).—When a few drops of 5 per cent. chromic acid solution is added to feebly acidified urine, the albumin is precipitated in flocks, even if present in but very small quantity. Phosphates and urates do not interfere with the test.

If bile pigments are present, the urine assumes an intense green colour on adding the chromic acid, but it is essential that the chromic acid be added drop by drop with constant agitation, otherwise the liquid becomes brownish-red, and the addition must be made the more carefully the larger the amount of the bile pigments present.

A. J. G.

General and Physical Chemistry.

Study of Chemical Reactions in a Liquid Mass by means of the Index of Refraction. By C. FÉRY (*Compt. rend.*, 115, 1309—1312).—By comparing the indices of refraction of solutions containing two substances which are capable of acting one on the other with those calculated on the assumption that the observed index should be given by the mean of those of the two constituents, it is possible to gain evidence of the occurrence of chemical change in solution. Thus, in a solution containing sodium hydroxide and nitric acid, it was found that the maximum deviation of the observed from the calculated values occurred in a solution containing 8 parts of NaOH and 12·31 parts of HNO_3 in 100 of water, the ratio 12·31/8·00 being nearly equal to that of HNO_3/NaOH . In the case of mixtures of alkalis with sulphuric acid, there are two points at which changes occur in the curve for the indices of refraction, one corresponding with a mixture that would form the acid, and the other to one that would form the normal salt. The curve for phosphoric acid has three such points. In cases where no chemical action occurs, the observed and calculated values for the indices of refraction are found to coincide, the curve for the indices of refraction of such mixtures being a continuous straight line.

In addition to the points where the maximum deviation of the observed from the calculated values occurs, the author has observed certain other slight changes and breaks in the indices of refraction curves. These breaks he attributes to the formation of hydrates by the union of water with the substances under examination. A special study of this point, in the case of sulphuric acid solutions, showed that such breaks occurred with solutions corresponding with the hydrates $\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$; $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$; $\text{H}_2\text{SO}_4, 1\frac{1}{2}\text{H}_2\text{O}$; and $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$.

H. C.

Spectrum of Liquid Oxygen and Refractive Indices of Liquid Oxygen, Nitrous Oxide, and Ethylene. By G. D. LIVEING and J. DEWAR (*Phil. Mag.* [5], 34, 205—209).—The hot pole of an electric arc was viewed through a column of 3 inches of liquid oxygen with a spectroscope having two calcite prisms of 30° and one of 60° . The red potassium lines were used as reference rays. Instead of the solar A, a band was observed having a sharp edge on the less refrangible side and fading away gradually on the more refrangible side. The sharp edge did not coincide with the sharp edge of A, the wave-length being about $\lambda 7660$. No band corresponding with B was observed, but through a thickness of 6 inches of liquid oxygen a faint band appeared, which had precisely the same character as A, the wave-length of the sharp edge being $\lambda 6905$. Liquid oxygen is distinctly blue, this colour, apparently, not being due to ozone. Ozone explodes at a low temperature with great violence.

The refraction constant, $\frac{\mu_D - 1}{d}$, for oxygen at its boiling point, -182° , is 0.1989, and its refraction equivalent 3.182. For the formula $\frac{\mu^2 - 1}{(\mu^2 + 2)d}$ the corresponding values are 0.1265 and 2.024.

For liquid nitrous oxide at -90° , $\frac{\mu_D - 1}{d} = 0.2634$ and $\frac{\mu^2 - 1}{(\mu^2 + 2)d} = 0.163$, giving the molecular refractions 11.587 and 7.163 respectively. Ethylene gives at -100° , $\frac{\mu_D - 1}{d} = 0.627$ and $\frac{\mu^2 - 1}{(\mu^2 + 2)d} = 0.384$. The corresponding numbers for gaseous ethylene are 0.578 and 0.385.

J. W.

Phosphorescent Zinc Sulphide as a Photometric Standard.

By C. HENRY (*Compt. rend.*, 116, 98—99).—Within somewhat wide limits, which correspond with luminous saturation, the quantity of light emitted by a surface of phosphorescent zinc sulphide at a given instant is independent of the distance of the exciting magnesium, of the time of illumination, and the thickness of the layer of zinc sulphide.

The law of the loss of luminosity of phosphorescent zinc sulphide is always the same, although the sulphide may have been prepared by different workers at different times, and although the initial intensity of luminosity may not be the same. This law is represented by the expression $i^m(t + c) = K$, the value of m being 0.598 and of c , 28.35. The law holds good also for thicknesses of the layer of sulphide varying from 0.45 mm. to 0.9 mm. Within these limits of thickness the maximum intensity of the phosphorescence is independent of the length of magnesium ribbon burnt and of the distance at which it is held, provided that the length of ribbon is not less than 15 cm. and the distance is not greater than 28 cm.

C. H. B.

Thermoelectric Phenomena between two Electrolytes. By

H. BAGARD (*Compt. rend.*, 116, 27—29; compare Abstr., 18.2, 1037).—The method previously described has been applied to the investigation of the behaviour of couples formed by two solutions of zinc sulphate of different concentrations. For a given temperature, the electromotive force is greater the greater the difference between the degrees of concentration of the two solutions. The neutral point is also higher the greater the difference of concentration. The law of intermediate substances and the law of intermediate temperatures were both found to hold good.

C. H. B.

The Ignition Point. By A. MITSCHERLICH (*Ber.*, 26, 160—164; compare *Ber.*, 9, 314).—This paper forms one of a series the author is about to publish on the combustion point and ignition point, the former term denoting the temperature at which combination commences and the latter the temperature at which it takes place with evolution of light; the combustion points of gaseous mixtures will be first dealt with, and afterwards those of liquids and solids. The present

paper gives the results obtained with a mixture of hydrogen and oxygen.

The mixture of these gases was passed through a combustion tube of 4.2 mm. diameter heated in a crucible, the temperature of which was measured by a specially constructed pressure thermometer. The ignition point was found throughout a long series of experiments to be 671° , and is independent of the methods by which the gases are prepared so long as they are pure, of the action of light, of long continued heating if the temperature is below the combination point, and of the motion of the gases. The product of combination formed, if the mixture is only heated somewhat above the combustion point, considerably affects the ignition point, and the mixture must therefore be heated as quickly as possible to the latter temperature.

H. G. C.

Diffusion Phenomena with Precipitate Membranes. By P. WALDEN (*Zeit. physikal. Chem.*, **10**, 699—732).—To obtain membranes suitable for diffusion experiments the following plan was adopted. The tubes taken were about 50 mm. in length and 10 mm. in diameter. After closing the upper end with the thumb, the lower end was dipped into a warm 20 per cent. solution of gelatin, containing ammonium chromate. After carefully draining off the excess of gelatin, a membrane is left closing the end of the tube, which hardens and becomes insoluble on exposure to light. To obtain a precipitate within such a membrane the tube is filled with a solution of one of the precipitants and is then placed in a solution of the other, when they meet by diffusion and form the precipitate in the membrane.

The behaviour of a large number of different precipitate membranes towards salt solutions was examined, the author giving a general record of his results in tabular form. Both electrolytes and non-electrolytes diffuse through precipitate membranes. The acids and salts of monacid bases or monobasic acids diffuse with greatest readiness, salts of polyacid bases or polybasic acids only diffusing slowly and with difficulty or even not at all. The diffusibility of different compounds depends rather on the nature and the arrangement of their components than on the number or weight of the atoms, and is not directly related to the diffusibility of the ions in the case of electrolytes. At the same time, quantitative measurements with salts of the alkali metals show that both the positive and negative ions pass through the membrane in quantities that are in the order of their electrical velocities of transference. The numbers in the case of the free acids are not proportional to their affinity coefficients, although acids having the same affinity coefficients are found to diffuse through the membrane in equivalent quantities.

H. C.

Influence of the Concentration of the Ions on the Intensity of Colour of Solutions of Salts in Water. By C. E. LINEBARGER (*Amer. J. Sci.* [3], **44**, 416—418).—As the intensity of the colour of a solution depends in a great measure on the number of ions contained in it, and the electrical conductivity of salt solutions increases as the temperature rises, if a coloured solution is heated, its colour

should deepen. Abundant experimental proof of this is to be found in Gladstone's investigation, "On the Effect of Heat on the Colour of Salts in Solution" (*Phil. Mag.*, **14**, 423). H. C.

Determination of Molecular Weight at the Critical Point. By P. A. GUYE (*Ann. Chim. Phys.* [6], **26**, 97—112).—The substance of this paper has been previously published (compare Abstr., 1891, 1411). F. S. K.

Molecular Dissymmetry. By P. A. GUYE (*Ann. Chim. Phys.* [6], **25**, 145—226).—The author explains at considerable length his views on the nature of molecular dissymmetry, and gives a list of the optically active substances which he has examined (compare Abstr., 1892, 399, 758). F. S. K.

Simplification in the Process of Fractional Distillation. By A. TIGERSTEDT (*Ber.*, **26**, 172).—In order to ascertain the weight of the fractions passing over at different temperatures when the separation of the fractions is not required, the author recommends the placing of the receiver on a small balance such as is frequently employed for letters, in which the weight is shown by means of a pointer and scale. The position of the pointer at the different temperatures is then read off and the weight of each fraction thus ascertained. H. G. C.

Inorganic Chemistry.

Preparation of Pure Iodine. By C. MEINEKE (*Chem. Zeit.*, 1219—1220; 1230—1233).—Musset has recommended the following process:—A suitable quantity of iodine is put into a beaker and covered with a concentrated solution of potassium iodide. Heat is applied until the iodine has fused. After cooling, the cake of iodine is washed, and is then free from chlorine.

The author has improved the process, and has succeeded in also removing any cyanogen. Instead of potassium iodide alone, he prefers a mixture of a solution of calcium chloride (sp. gr. 1.35) and a little potassium iodide, with a few drops of hydrochloric acid. The iodine is then sublimed twice, the first time with the addition of a little barium oxide. Absolutely pure iodine is obtained in this manner.

L. DE K.

Physical Constants of Fluorine. By H. MOISSAN (*Ann. Chim. Phys.* [6], **25**, 125).—The author gives a *résumé* of his recent work on the physical constants of fluorine (compare Abstr., 1890, 208, 329); fluorine does not liquefy at -95° under the ordinary atmospheric pressure. F. S. K.

Action of Sulphur in presence of Water on Salts of Polybasic Acids. By J. B. SENDERENS (*Bull. Soc. Chim.* [3], 7, 511—516).—In a former paper (Abstr., 1892, 770), the author dealt with the action of sulphur in presence of water on salts of monobasic acids. He now states that in the case of nickel and cobalt oxides there is first formed a sulphate and a thiosulphate, but as the reaction proceeds the amount of the latter gradually becomes less until it is reduced to *nil*. He then proceeds to give the results of similar observations on the salts of polybasic acids. Sulphur is without action on boiling solutions of alkali sulphates and oxalates; solutions of bibasic tartrates and tribasic citrates which exhibit alkaline reactions are completely neutralised when boiled with sulphur and water; it is concluded that tartaric acid has a strong acidic function and a medium one, and citric acid two strong acidic functions and a medium one. Carbonates and borates are completely decomposed when boiled with sulphur and water, so that the acidic functions of the corresponding acids are feeble. Tribasic alkali phosphates behave as if they had a function 1.5 times that of a strong acid, and the corresponding calcium and barium derivatives as though they had two strong acidic functions. Tribasic silver phosphate is completely reduced when boiled with sulphur and water, as are likewise the copper salts $\text{Cu}_3(\text{PO}_4)_2$, CuHPO_4 , $\text{CuH}_2(\text{PO}_4)_2$, but the phosphates of lead, nickel, and cobalt remain unaltered. The phosphates, therefore, behave very like the sulphates, and phosphoric acid would seem to have three strong acidic functions. On boiling trisodium arsenate with sulphur and water, it is converted into a thiosulphate and a polysulphide; the latter decomposes with the evolution of hydrogen sulphide, which reacts with the unaltered arsenate, forming thioarsenate and oxythioarsenate. Sodium arsenite gives rise to a polysulphide which decomposes into hydrogen sulphide, forming arsenious sulphide, and finally sodium sulpharsenite. Potassium chromate is thus decomposed: $-6\text{K}_2\text{CrO}_4 + 15\text{S} + 9\text{H}_2\text{O} = 6\text{Cr}(\text{OH})_3 + 5\text{K}_2\text{S}_2\text{O}_3 + \text{K}_2\text{S}_5$; the polysulphide then decomposes into hydrogen sulphide and potassium thiosulphate. In the case of potassium dichromate the reaction is as follows: $-7\text{K}_2\text{Cr}_2\text{O}_7 + 10\text{S} + \text{Aq} = 2(\text{CrO}_3, 3\text{Cr}_2\text{O}_3) + 4\text{K}_2\text{SO}_4 + 3\text{K}_2\text{S}_2\text{O}_3 + \text{Aq}$. The compound $\text{CrO}_3, 3\text{Cr}_2\text{O}_3$ is a brown precipitate. The last-named results are in agreement with the observations of Sabatier (Abstr., 1886, 973). Potassium manganate is thus decomposed: $-2\text{K}_2\text{MnO}_4 + 5\text{S} + 2\text{H}_2\text{O} = \text{Mn}_2\text{O}_3, \text{H}_2\text{O} + 2\text{K}_2\text{S}_2\text{O}_3 + \text{H}_2\text{S}$ whilst in the case of potassium permanganate, potassium sulphate and manganese dioxide are obtained.

A. R. L.

Tellurium. By E. PRIWOZNIK (*Chem. Centr.*, 1892, ii, 962; from *Österr. Zeit. Berg. Huttenwes.*, 44, 529—531).—Crude tellurium is fused in a bulb tube of difficultly fusible glass in a stream of hydrogen gas. The hydrogen serves not only for the decomposition of tellurous oxide, which prevents the satisfactory fusion of the tellurium, but also removes any selenium by converting it into hydrogen selenide. Tellurium can also be distilled in a stream of hydrogen, best from a porce'ain boat placed in a tube of hard glass; it is deposited

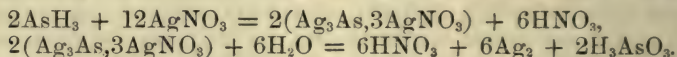
on the cold portion of the tube, partly in lustrous drops, partly in spear-shaped prisms, having numerous striated and hollowed faces. Tellurium has sp. gr. 6.2459 at 18.2°. In determining the sp. gr. it is necessary to boil carefully with water, in order to displace any air from the fine cavities which generally occur in the regulus.

A. J. G.

Nitrous acid in Nitric acid. By L. MARCHLEWSKI (*Zeit. anorg. Chem.*, **2**, 18—20; compare Abstr., 1892, 113; and Montemartini, *Real. Accad. Linc.*, 1892, i, 63—67).—The author criticises Montemartini's results, and shows that they do not bear the interpretation the latter puts on them, his method, indeed, being incapable of detecting any but a relatively large quantity of nitrous acid, in the case when nitrogen peroxide is also present.

C. F. B.

Action of Hydrogen Arsenide, Antimonide, and Phosphide on Silver Nitrate. By D. VITALI (*L'Orosi*, 1892, 397—411).—The action of hydrogen arsenide on aqueous silver nitrate has been considered by Lassaigne (*J. Chem. Med.*, **16**, 685) to proceed in accordance with the equation $2\text{AsH}_3 + 12\text{AgNO}_3 + 6\text{H}_2\text{O} = 12\text{HNO}_3 + 6\text{Ag}_2 + 2\text{H}_3\text{AsO}_3$; the reaction, however, occurs in two stages, as follows:—



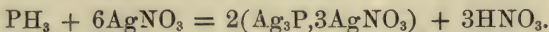
Marchlewski (Abstr., 1891, 1154) supposed that any representation of this reaction which involves the simultaneous liberation of silver and nitric acid must be untrue, for he found that dilute nitric acid dissolves finely divided silver; he further stated that arsenious acid reduces dilute nitric acid with formation of nitrous acid, which greatly assists the action of nitric acid on silver. The author, however, finds that on passing hydrogen arsenide into neutral silver nitrate solution, the amount of silver nitrate decomposed and the quantities of free nitric and arsenious acids subsequently remaining in the solution are in the proportions indicated by the above equations; he was unable to detect the presence of nitrous acid. Marchlewski's objections to Lassaigne's equation are therefore invalid, and Houzeau's method for determining arsenic acid, depending on this reaction, is an exact one.

Several chemists have stated that silver nitrate solution is reduced on passing a current of pure hydrogen through it; this the author shows to be due to impurities present in the gas, silver nitrate solution being extremely sensitive to hydrogen arsenide, antimonide, or phosphide.*

The action of hydrogen antimonide on aqueous silver nitrate is in all respects analogous to that of the arsenide; in this case, however, the antimonious acid, being insoluble, separates with the silver, from which it may be extracted by hydrochloric acid. The author has followed the course of the action by quantitative determinations.

* The author seems to be unaware that Dr. W. J. Russell has shown conclusively that hydrogen precipitates metallic silver from a solution of silver nitrate (this *Journal*, 1874, 3).—EDITORS.

The action of nearly pure hydrogen phosphide on concentrated silver nitrate solution results in an explosion; if the gas be considerably diluted with hydrogen, the first phase of the reaction is expressed by the equation



The yellow double compound formed is more stable than those containing arsenic or antimony, but blackens on adding water, leaving a mixture of silver and silver phosphide, which evolves hydrogen phosphide on treatment with zinc and hydrochloric acid. The yellow substance soon decomposes on exposure to the air, leaving metallic silver. Dilute solutions of silver nitrate yield at once the black mixture of silver and silver phosphide, and the solution is found to contain nitric, nitrous, phosphoric, and hypophosphorous acids. This reaction would be useless as the basis of a method for determining phosphorus similar to those afforded by the action of hydrogen arsenide and antimonide on silver nitrate solution. W. J. P.

Atomic Weight of Boron. By E. RIMBACH (*Ber.*, **26**, 164—171).—The author has redetermined the atomic weight of boron from the amount of sodium contained in crystalline borax, the estimation of the sodium being made by titration with hydrochloric acid of known strength, using methyl-orange as indicator. The latter is not changed by boric acid, and only undergoes change when the whole of the sodium in the borax has been converted into the chloride.

The borax was prepared from pure boric acid by treating it with the theoretical quantity of pure sodium carbonate, recrystallising the product three times, and drying in the air until the loss of weight was almost inappreciable; the hydrochloric acid employed was carefully purified, and all titrations carried out in vessels made of glass which was only attacked very slightly by water. The mean result showed that the atomic weight of boron ($\text{O} = 16$, $\text{H} = 1.0032$) is 10.945, which agrees closely with the number recently obtained by Ramsay and Aston (*Trans.*, 1893, 207), but differs by 0.1 from that found by Abrahall (*Trans.*, 1892, 650). H. G. C.

Silver. By M. C. LEA (*Amer. J. Sci.* [3], **44**, 444—446).—Aqueous ammonia has a distinct solvent action on silver reduced from the nitrate by sodium hydroxide and lactose, or reduced from the chloride by cadmium and hydrochloric acid. If the solutions are evaporated to dryness on a water-bath, brown-black, non-explosive residues are left, which dissolve almost completely in acetic acid, leaving a small quantity of metallic silver which has probably been reduced by organic matter in the ammonia. The acetic acid solution contains a considerable quantity of silver, and it is evident that the silver dissolves in the form of oxide.

Aqueous ammonia has no solvent action on silver when air is completely excluded.

Almost any form of finely divided silver is distinctly soluble, contrary to the usual statement, in sulphuric acid diluted with four or five times its bulk of water, but with more dilute acid the different

forms of the metal behave very differently. The form most easily attacked is that obtained by reduction with an alkali hydroxide and lactose, and this is distinctly soluble in sulphuric acid diluted with 100 times its volume of water. Acid of this strength has no action at all on silver reduced from the chloride by cadmium.

Nitric acid of sp. gr. 1.40, diluted with water to 10 volumes and allowed to remain in contact with finely divided silver for an hour, dissolves only a minute trace of the metal. Hydrochloric acid of sp. gr. 1.20 is entirely without action on metallic silver, and this is true also of acetic acid.

Normal silver, even when in a fine state of division, is not attacked in the slightest degree by perfectly neutral copper nitrate solution obtained by the action of copper sulphate on barium nitrate, even after 15 hours contact. On the other hand, silver readily reduces cupric chloride with formation of the purple photochloride, and if the cupric salt is present in slight excess, the change is so complete that the product is quite insoluble in nitric acid. Metallic mercury instantly reduces silver nitrate, but silver, on the other hand, reduces mercuric chloride.

A solution of ferric alum readily dissolves silver at the ordinary temperature, with production of a ferrous salt, and if the ferric compound is in excess, the whole of the silver is dissolved. When ferrous sulphate solution is mixed with successive quantities of silver oxide until a fresh quantity of the latter is no longer affected, the whole of the iron is precipitated, and a black product is obtained which is probably the compound $\text{Ag}_4\text{O}, 2\text{FeO}, \text{Fe}_2\text{O}_3$, obtained by H. Rose in the same way.

When a solution of ammonium ferric alum is mixed with a large excess of finely divided silver in a well closed vessel and allowed to remain for several days, with frequent agitation, the liquid acquires a deep red colour, which may persist for several days, but then gradually disappears, the solution becoming greenish, although it still contains a considerable quantity of ferric salt. It follows that the reducing action of silver on ferric salts is limited and ceases before reduction is complete, even when the silver is present in large excess.

C. H. B.

Silver Chloride. By M. C. LEA (*Amer. J. Sci.* [3], **44**, 446—447).—Acworth has observed that when silver chloride is heated at 220° it becomes insensitive to light. The author considers that this result is due to complete expulsion of the moisture. Silver chloride, after being dried in hot air, always loses from 0.5 to 1.0 milligram per gram when melted.

C. H. B.

Action of Dried Hydrogen Chloride on Iceland Spar. By R. E. HUGHES and F. R. L. WILSON (*Phil. Mag.* [5], **34**, 117—120).—Hydrogen chloride was passed over copper turnings and through tubes containing pumice moistened with sulphuric acid, and finally pumice and phosphoric anhydride. The gas thus purified and dried was then passed over a weighed quantity of Iceland spar at 130° for about an hour, at the end of which time the spar was again weighed.

No practical increase in weight was noted. Moist hydrogen chloride occasioned an increase of 0.02 gram on 0.69 gram of Iceland spar.

J. W.

Constitution of Bleaching Powder as elucidated by its Dissociation. By J. MIJERS (*Rec. Trav. Chim.*, **11**, 76—83).—The author's results lead him to the view that bleaching powder is not identical with the compound obtained by Lunge by passing a current of hypochlorous anhydride over hydrated calcium chloride. He regards bleaching powder as a compound of calcium hydroxide with chlorine, $\text{Ca}(\text{OH})_2\text{Cl}_2$; and to the active compound he ascribes the formula CaOCl_2 . It is only possible to prepare bleaching powder free from uncombined calcium hydroxide at very low temperatures.

A. R. L.

Note.—The author does not allude to Dreyfus' experiments (*Abstr.*, 1885, 19), who arrives at a different conclusion (compare, however, Lunge and Schoch, *Abstr.*, 1887, 70).

A. R. L.

Complete Elimination of Barium from Strontium Salts. By BARTHE and FALIÈRES (*Bull. Soc. Chim.* [3], **7**, 473—475).—A reply to the criticisms of Cannepin (*Union pharmaceutique*, 1892, 1), on the authors' process (*Abstr.*, 1892, 1277).

A. R. L.

Magnesium Nitride. By S. PASCHKOWEZY (*J. pr. Chem.* [2], **47**, 89—94).—The author has carried out Merz's method for making magnesium nitride (*Abstr.*, 1892, 409) on a somewhat larger scale. 20—25 grams of powdered magnesium was spread in a layer 0.9—1 m. long in a combustion tube of 11—12 mm. diameter, and heated in a current of well dried ammonia. The nitride thus produced contained 27.84 per cent. of nitrogen (theory = 28 per cent.). The orange surface-colour appears when the heating is strongest, but has no appreciable influence on the percentage of nitrogen. The nitride was also produced by the direct absorption of nitrogen by the hot magnesium.

A. G. B.

Purification of Arsenical Zinc. By H. LESCEUR (*Compt. rend.*, **116**, 58—60).—Fusion of zinc with potassium nitrate removes sulphur and phosphorus, but does not remove arsenic and antimony, whilst fusion with ammonium chloride or magnesium chloride expels arsenic and antimony, but does not affect the sulphur and phosphorus. In order to obtain pure zinc for toxicological purposes, both modes of treatment must be applied, the metal being first fused with potassium nitrate, and afterwards with a chloride or *vice versâ*. Zinc chloride is preferable to either ammonium or magnesium chloride for this purpose. The double treatment removes arsenic, antimony, sulphur, and phosphorus, but does not, of course, remove metals such as copper, lead, or iron.

C. H. B.

Preparation of Acicular Basic Zinc Nitrate. By A. TERREIL (*Bull. Soc. Chim.* [3], **7**, 553—554).—A solution of zinc nitrate is boiled for an hour or two with an excess of metallic zinc, and then

evaporated at a gentle heat to a syrup, which solidifies on cooling. The mass is now extracted with cold water, which dissolves the normal nitrate, leaving the basic nitrate in the form of delicate needles of the composition $5\text{ZnO}, \text{N}_2\text{O}_5 + 5\text{H}_2\text{O}$.

These needles, when heated, lose first water and then nitric anhydride, leaving a pseudomorph of zinc oxide, which retains a slight yellow colour when quite cool. A certain quantity of ammonium nitrate is formed and nitric oxide is evolved when the basic nitrate is treated with nitric acid.

A. R. L.

Dehydration of Copper Hydroxide and certain of its Basic Compounds in the presence of Water. By W. SPRING and M. LUCION (*Zeits. anorg. Chem.*, 2, 195—220).—Copper sulphate was precipitated in the cold with alkali hydroxide, and the blue hydrated oxide, after washing, suspended in water. Equal quantities were then introduced into a flask containing either pure water or a solution of one of the salts mentioned below. It is found that the freshly-precipitated compound is only completely dehydrated in contact with pure water at 15° after 9 months, at 30° after 86 hours, at 45° after 38 hours, and the hydrated oxide cannot exist above 54° . The dehydration proceeds the more slowly the longer the time which has elapsed since its preparation. The freshly-precipitated blue compound has the composition $\text{CuO} + 2\text{H}_2\text{O}$, and this hydrate, after being for some hours in contact with water at 15° , is converted into the brown monohydrate $\text{CuO} + \text{H}_2\text{O}$, which is then further dehydrated more slowly. At temperatures of 30° and 45° , and in the presence of certain salts, the dehydration is expedited; it, however, proceeds more slowly after reaching the monohydrate stage. The salts employed were the following:—Sodium and potassium hydroxides, sodium and potassium chlorides, potassium bromide, potassium iodide, barium chloride, zinc chloride, sodium sulphate, magnesium sulphate, manganese sulphate, and potassium nitrate. The electrolytic dissociation of these salts appears to have some connection with their dehydrating powers, but the exact relation between the dehydrating powers and the osmotic pressures of the salts could not be traced from the data at hand, which were complicated in certain cases by the formation of intermediate basic salts. Thus, in the case of the haloïd salts, colloïdal compounds of the general formula $\text{Cu}_2\text{X}_2, \text{CuO} + 3\text{H}_2\text{O}$ result. This formation of cuprous compounds from cupric without the intervention of a reducing agent is thus explained:—When pure hydrated copper oxide is triturated with a solution of potassium bromide at 25° , after a while an evolution of oxygen takes place, and the filtrate is found to contain hydrogen peroxide. The following reactions occur. (1) $3\text{Cu}(\text{OH})_2 + 2\text{KBr} = \text{Cu}_2\text{Br}_2, \text{Cu}(\text{OH})_2, \text{H}_2\text{O} + \text{K}_2\text{O}_2, \text{H}_2\text{O}$. (2) $\text{K}_2\text{O}_2, \text{H}_2\text{O} = 2\text{KOH} + \text{O}$. When hydrated copper oxide is mixed with a solution of copper chloride, and the excess of the latter removed by dialysis, the compound $\text{Cu}_2\text{Cl}_2, \text{CuO}, 3\text{H}_2\text{O}$ is directly synthesised. The author finally discusses the important geological bearing of these results.

A. R. L.

Molecular Weight of "Gadolinium Oxide." By A. E. NORDENSKIÖLD (*J. pr. Chem.* [2], **47**, 1—27; compare Abstr., 1887, 109).—By the term "gadolinium oxide," the author implies that group of earthy oxides which are precipitated from the solution of their sulphates by ammonia and by oxalic acid, but not by an excess of normal potassium sulphate. A new series of determinations of the equivalent of this group of oxides has been made, and a list of the values obtained for the oxide from 54 minerals is given. These only vary from 275·8 to 247·9, or $\pm 5\cdot4$ per cent. from the mean, 262, notwithstanding the fact that the equivalents of the individual oxides contained in the "gadolinium oxide" vary between 136 and 394, if scandium be included, or between 227 and 394 if this be excluded. It is notable that in most cases where different minerals contain closely allied elements, a given mineral will contain only one of these elements, or at all events chiefly one with small quantities of another or others. For example, the determination of the equivalent of the earthy oxide in a calcium, barium, or strontium mineral will almost always approximate very closely to the equivalent of lime, baryta, or strontia. This is not so with the minerals containing the group of gadolinium oxides. All determinations of the equivalent in question made by previous observers which are, in the author's opinion, trustworthy agree with the limits given above. A list of these other determinations is given, and the author's methods are described.

A. G. B.

The Alloys of Iron and Tin. By W. P. HEADDEN (*Amer. J. Sci.*, **44**, 464—468).—From a study of the formation of the alloys of tin and iron, the author concludes that there is a series of iron stannides, of which he obtained the following members: FeSn_2 , Fe_2Sn_3 , $\text{Fe}_3\text{Sn}_{14}$, Fe_4Sn_5 , Fe_5Sn_6 , FeSn , Fe_3Sn , Fe_4Sn , and Fe_9Sn . Some of these have been described before; but the published descriptions assign to them properties some of which differ widely from those observed by the author.

B. H. B.

Roussin's Salt. By L. MARCHLEWSKI and J. SACHS (*Zeit. anorg. Chem.*, **2**, 175—181).—The author has confirmed the formula $\text{Fe}_4(\text{NO})_7\text{S}_3\text{K} + \text{H}_2\text{O}$, assigned by Pavel (Abstr., 1883, 297) to Roussin's salt, by analysis, and by a determination of the molecular weight by Beckmann's boiling point method in ethereal solution. The compounds analysed by Roussin and by Rosenberg were impure, but on adding thallium sulphate to an aqueous solution of these preparations, a salt separates, which, when crystallised as rapidly as possible from alcohol in a vacuum, has the composition $\text{Fe}_4(\text{NO})_7\text{S}_3\text{Ti} + \text{H}_2\text{O}$; it is very sparingly soluble in water, and decomposes on protracted heating with it.

A. R. L

Cobalt. By H. REMMLER (*Zeit. anorg. Chem.*, **2**, 221—234).—The material employed in this research was prepared from 1200 grams of cobalt chloride. The salt was dissolved in the smallest possible quantity of distilled water, and the filtered solution warmed with bromine water (1 litre), and potassium hydroxide added, until the mixture was distinctly alkaline; it was then warmed for two hours,

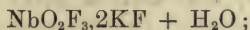
and the hydrated oxide washed by decantation 15 times, with about 6 litres of water, and finally thrown on to a filter, and the washing continued until the filtrate was free from chloride. The hydrated oxide was then treated with successive quantities of ammonia, which dissolves it slowly. In this way in the space of nine months, 25 fractions were obtained. The ammoniacal extracts were then purified, and finally converted into cobaltous oxide, and thence, by ignition of the latter in a current of dry carbonic anhydride, into cobaltic oxide. The fractions were found on qualitative examination to be free from iron, manganese, and nickel. Atomic weight determinations were made by weighing the amounts of cobalt obtained by igniting the oxide representing the various fractions in a current of hydrogen. The results lie between 59.53 and 58.3, differences far beyond the experimental error of the method, so that the author comes to the same conclusion as Krüss and Schmidt, namely, that cobalt purified by the ordinary method is not a homogeneous substance.

A. R. L.

Determination of the Atomic Weight of Nickel. By G. KRÜSS and F. W. SCHMIDT (*Zeit. anorg. Chem.*, 2, 235—254).—Continuing their experiments (Abstr., 1889, 349 and 1114), the authors have not succeeded in isolating a new element in the pure state from nickel; they find, however, that the metal prepared by carefully reducing the oxide in a current of hydrogen is not homogeneous, even when it gives the usually accepted atomic weight 58.6. The fact cited by Winkler (Abstr., 1889, 760) that nickel which has not been fused imparts slight alkalinity to water is discussed, and the following experiment is described. A quantity of the nickel used for the atomic weight determination by Zimmermann (Abstr., 1886, 596) was warmed with water on the water-bath for almost a year; from the resulting greenish-coloured solution, a small quantity of a substance was isolated after conversion into sulphate. Two solutions containing known quantities of the latter were precipitated with potassium hydroxide, and the oxide weighed; from these data, the substance appears to have been derived from an element having an equivalent between 35 and 45. The process cannot, however, be employed for the quantitative separation of the impurity, and numerous other fruitless attempts were made to obtain pure nickel. Ultimately the following experiments were conducted. Nickel oxide, rendered free from all known impurities with the exception of cobalt, was reduced in a current of pure dry hydrogen, at as low a temperature as possible, and subsequently treated with carbonic oxide. The gases which were evolved were passed through a series of flasks containing aqua regia, whereby the nickel carbonyl was decomposed, and the metal retained as chloride. The residue which had not volatilised was then treated successively with hydrogen and carbonic oxide as before, and this was repeated 10 times, so that 10 fractions were obtained, which were converted into metal. Atomic weight determinations were then made with each of the fractions, as follows. A portion of the metal was converted into the oxide, and the weight of metal obtained on reducing the latter with hydrogen ascertained. The metal was also quantitatively converted

into oxide, and the oxide again reduced. The results differed among themselves to an extent beyond the experimental error of the methods. The authors conclude, however, that the atomic weight of nickel is at most 58.1, and it would seem that a foreign metal, whose atomic weight is greater than 58.5, is present in nickel, and that when the oxide is reduced in a current of hydrogen, this element is in part volatilised. The residual metal left from the tenth fraction was freed from cobalt and converted into five fractions as oxide. The latter gave atomic weights varying between 59.17 and 64. A. R. L.

Action of Hydrogen Fluoride on certain Fluorides and Oxyfluorides. By A. PICCINI (*Zeit. anorg. Chem.*, **2**, 21—24; compare this vol., ii, 124).—The author has now prepared *potassium fluoroxyper tungstate*, $\text{WO}_3\text{F}_2 \cdot 2\text{KF} + \text{H}_2\text{O}$; *fluoroxyper niobate*,



and *fluoroxyper tantalate*, $\text{TaO}_2\text{F}_3 \cdot 2\text{KF} + \text{H}_2\text{O}$. These compounds were obtained in the same way as the potassium fluoroxypermolybdate, $\text{MoO}_3\text{F}_2 \cdot 2\text{KF} + \text{H}_2\text{O}$, previously described, and resemble that substance closely in their properties. The substances from which they were prepared, $\text{WO}_3\text{F}_2 \cdot 2\text{KF} + \text{H}_2\text{O}$, $\text{NbOF}_3 \cdot 2\text{KF} + \text{H}_2\text{O}$, and $\text{TaF}_5 \cdot 2\text{KF}$ respectively, were themselves obtained from potassium tungstate, niobic acid, and tantallic acid respectively, by treatment with hydrofluoric acid. C. F. B.

An Acid Potassium Platonitrite. By M. VÈZES (*Compt. rend.*, **116**, 99—102).—When a solution of potassium platonitrite containing any free acid, or an acid solution of a halogen derivative of the platonitrite, is concentrated, a new compound is formed and separated as a red crust made up of very slender needles.

In order to obtain this product in considerable quantity, a warm, concentrated solution of the platonitrite is mixed with an exactly equivalent quantity of sulphuric acid, so that the composition of the mixture is $\text{K}_2\text{Pt}(\text{NO}_2)_4 + \text{H}_2\text{SO}_4$. The green solution, when strongly concentrated by heat, gives off nitrogen oxides, and on cooling deposits slender, red needles which can be recrystallised from hot water. They have the composition $\text{K}_2\text{H}_4\text{Pt}_3\text{O}(\text{NO}_2)_6 + 3\text{H}_2\text{O}$, lose their water of crystallisation in dry air or at 100° , and decompose with effervescence when strongly heated.

Titration of a solution of the salt with potassium hydroxide, using litmus as an indicator, shows that neutrality is reached when 1 mol. of potassium hydroxide has been added to 1 mol. of the salt, and hence the formula of the latter would be $\text{Pt}_3\text{O}(\text{NO}_2)_6\text{K}_2\text{H}$. If, however, phenolphthaleïn is used as the indicator, 4 mols. of the alkali are required to produce neutrality, and hence the formula of the salt would be $\text{K}_2\text{H}_4\text{Pt}_3\text{O}(\text{NO}_2)_6$, as already stated. Further experiments are in progress with a view to decide this question. C. H. B.

Rhodium Salts. By T. WILM (*Zeit. anorg. Chem.*, **2**, 51—63).—In addition to the two double salts (1) $\text{Rh}_2\text{Cl}_6 \cdot 6\text{NH}_4\text{Cl} + 3\text{H}_2\text{O}$, and (2) $\text{Rh}_2\text{Cl}_6 \cdot 4\text{HCl} + 2\text{H}_2\text{O}$, the author previously (*Abstr.*, 1884, 660;

Ber., 16, 3033) described a third, (3) $\text{Rh}_2\text{Cl}_4 \cdot 8\text{NH}_4\text{Cl} + 7\text{H}_2\text{O}$. He now confirms Leidié's conclusion (*Bull. Soc. Chim.* [2], 50, 664), that this salt is really a chloronitrate, (4) $\text{Rh}_2\text{Cl}_4 \cdot 6\text{NH}_4\text{Cl} \cdot 2\text{NH}_4\text{NO}_3$. It is formed when much aqua regia is present in the solution. Water decomposes it, with formation of the salt (2); but, on the other hand, it is itself formed from this salt by the addition of ammonium nitrate. Curiously enough red, hexagonal plates, precisely similar to those of (4), are often obtained when the salts (1) and (2) crystallise out from solutions which do not contain any nitric acid, but these crystals are unstable, and rapidly change, usually into prismatic crystals of (2).

C. F. B.

Action of Chlorine and Carbonic Oxide on Iridium. By U. ANTONY (*Gazzetta*, 22, ii, 547—548).—The author has previously stated (Abstr., 1892, 1285) that iridium gives no trace of a volatile compound at 240° in a current of chlorine and carbonic oxide, whilst Mylius and Foerster (Abstr., 1892, 789) found that iridium is slightly volatile in such a gaseous mixture. Foerster (*Ber.*, 25, Ref. 441) attributes this seeming contradiction to a difference in the conditions under which the two sets of experiments were conducted; the author, however, cannot recognise this difference, and, after repeating his experiments, confirms his previous results.

W. J. P.

Mineralogical Chemistry.

Artificial Production of Mineral Sulphides. By H. N. WARREN (*Chem. News*, 66, 287).—By heating with potassium thiocyanate, litharge is converted into galena, even at a low red heat; whilst at the heat of fusion, the product has the same cleavage and almost the same sp. gr. as the native mineral. With the same reagent, iron oxide yields brilliant pyrites at a red heat, and Fe_2S_3 at a higher temperature; manganic oxide yields pyrolusite at bright redness; stannic and antimonious oxides yield the golden-yellow sulphides at low temperatures, and the ordinary sulphides at higher temperatures; and zinc oxide also yields a sulphide which exhibits phosphorescence in a marked degree.

D. A. L.

Aguilarite. By F. A. GENTH (*Amer. J. Sci.*, 44, 381—383).—The author gives analyses of several varieties of aguilarite: (a) irregular, flat particles in calcite; (b) small, capillary, needle- and wire-shaped individuals with small crystals, apparently hexagonal; (c) similar crystals, seen under the microscope to be made up of different minerals, the outer portion (1) being brittle, and the inner (2) malleable; and (d) solid dodecahedral crystals. The analytical results were as follows:—

	Ag.	S.	Se.	Cu.	Fe.	Sb.	As.	Total.
a.	79.41	5.93	13.96	0.50	—	—	—	99.80
b.	80.27	6.75	12.73	0.07	0.26	0.41	—	100.49
c1.	67.58	3.51	14.76	6.83	0.42	6.83	—	99.93
c2.	84.05	3.82	8.76	1.83	—	1.24	0.28	99.98
d.	84.40	11.36	3.75	0.49	—	—	—	100.00

B. H. B.

Metacinnabarite. By F. A. GENTH (*Amer. J. Sci.*, **44**, 333).—A specimen of metacinnabarite from San Joaquin, Orange Co., California, occurring in irregular particles in barytes, gave, on analysis, the following results:—

Hg.	S.	Cl.	Total.
85.89	13.69	0.32	99.90

It is remarkable that all the fragments that were examined showed the presence of chlorine.

B. H. B.

Danalite. By F. A. GENTH (*Amer. J. Sci.*, **44**, 385—386).—The occurrence of the rare mineral danalite, at Cheyenne Cañon, El Paso Co., Colorado, is described by the author. The fragment examined is part of a modified tetrahedron, with a sp. gr. of 3.626 to 3.661. Analysis yielded the following results:—

SiO ₂ .	BeO.	CuO.	ZnO.	FeO.	MnO.	S.	Ignition.
39.26	12.70	0.30	46.20	6.81	1.22	5.49	0.21

These results closely agree with the formula $(\text{Be}, \text{Zn}, \text{Fe}, \text{Mn})_7 \text{Si}_3 \text{O}_{12} \text{S}$.

In the same paper, the author gives analyses of rutile, of quartz resulting from the alteration of flesh-coloured orthoclase, and of yttrium-calcium fluoride from the same locality. He also gives analyses of löllingite from North Carolina, of altered zircon or cyrtolite from Mt. Antero, Colorado, of lepidolite from Japan, and of fuchsite from Habersham Co., Georgia.

B. H. B.

Phosphoric acid in Beryl. By F. C. ROBINSON (*Chem. News*, **63**, 297).—A sample of beryl, in colour grey to white with a mere trace of green, with a hardness of 7, and sp. gr. 2.627, lost, on drying at 100°, 0.33 per cent., and, on analysis, gave the following numbers:—

SiO ₂ .	Al ₂ O ₃ .	BeO.	P ₂ O ₅ .	(Na ₂ O, K ₂ O, Li ₂ O, Cs ₂ O).	Loss on ignition.	Total.
64.70	17.76	12.18	2.76	1.10	1.53	100.03

Regarding the phosphoric acid and alkalis as replacing a part of the beryllium, the molecular ratios for water, alumina, beryllium oxide, and silica are respectively 1, 2, 3, 12, showing that the mineral is a beryl. Other specimens of beryl have since been tested, and phosphoric acid has been detected in nearly every case, but in none of them in such a large proportion as 2.76 per cent.

D. A. L.

Mt. Joy Meteorite. By F. E. HOWELL (*Amer. J. Sci.*, **44**, 415—416).—This meteorite, the third largest in the United States, was found in November, 1887, in the township of Mt. Joy, Pennsylvania. The three largest dimensions of the meteorite are 11, 24, and $33\frac{1}{2}$ inches, and its weight is 847 lbs. Analysis yielded the following results:—

Fe.	Ni.	Co.	Cu.	P.	S.	Total.
93.80	4.81	0.51	0.005	0.19	0.01	99.325

The results of an examination of the magnetic properties shows that the meteorite as a whole acts as a mass of soft iron gaining polarity under the inductive action of the earth. B. H. B.

Meteorite of Grossliebenthal. By P. MELIKOFF and C. SCHWALBE (*Ber.*, **25**, 234—241).—The meteorite fell in November, 1881, at Grossliebenthal, near Odessa. It weighed over 8 kilos., and is covered with a black crust 1—1.5 mm. thick. The bulk of the meteorite is ash-grey and finely granular, and contains angular pieces of metal which are attracted by a magnet, and also pieces of iron sulphide and iron chromite. Its sp. gr. = 3.584 at 20°. An analysis gave the following results:—

H ₂ O.	SiO ₂ .	MgO.	CuO.	FeO.	MnO.	Al ₂ O ₃ .	Na ₂ O.	K ₂ O.	Fe ₂ S ₈ .
0.10	39.57	22.97	2.28	13.44	0.53	2.45	1.30	0.45	6.73
Fe ₁₁ Ni ₂ .		FeCr ₂ O ₄ .		P.	P ₂ O ₅ .	Cl.	Total.		
8.16		1.30		0.02	0.21	0.04	99.55		

It also contained traces of chromium and metals precipitated by hydrogen sulphide.

The silicates insoluble in hydrochloric acid had a sp. gr. = 3.179. The total silicates amount to 82.99 per cent., and consist of olivine 43.30 per cent., bronzite 26.87 per cent., and albite 12.82 per cent.

E. C. R.

Water and Sea-bottom Deposits of the Eastern Mediterranean. By K. NATTERER (*Monatsh.*, **13**, 873—896, 897—915).—In these papers, the author gives an account of a large number of analyses of sea water and sea-bottom deposits made during the voyages of the ship "Pola" in 1890 and 1891. The area investigated formed a quadrilateral, which lay between the islands of Corfu and Santorin on the European coast, and Ben-Ghâzi and Alexandria on the African coast. The tabulated results show that the substances dissolved in sea water were present in almost constant proportions in all the samples examined; but a noteworthy reduction in the quantity of bromine was observed in the neighbourhood of the African coast to the west of Alexandria. This reduction is, perhaps, to be attributed to the action of living plants, which store up bromine in the same way as they do iodine.

The author further gives the results of an analysis of the spring water used for supplying the Arsenal in the island of Crete.

G. T. M.

Physiological Chemistry.

Influence of Chloroform on Peptic Digestion. By A. BERTELS (*Virchow's Archiv*, 130, 497—511).—Chloroform exercises a destructive influence on Finzelberg's pepsin in artificial digestive mixtures, if it is added to saturation; air passed through the mixture has the same effect. But if fresh mucous membrane from the pig's stomach is used instead, neither chloroform nor air has the effect.

W. D. H.

Behaviour of Sterilised Milk towards Digestive Fluids. By ELLENBERGER and HOFMEISTER (*Expt. Stat. Record*, 4, 311; from *Molk. Zeit.*, 1892, No. 6).—When sterilised milk is consumed, there is no formation of cheese in the stomach, as is the case with fresh milk, and the action of the acids of the stomach is very incomplete. The sterilised milk remains in a more or less liquid state, and may pass too soon into, and even through, the intestines. Further experiments on the relative digestibility of raw and sterilised milk are wanted.

N. H. M.

Accumulation of Strontium Bromide in the Organism. By C. FÉRÉ and L. HERBERT (*Compt. rend. Soc. Biol.*, 1892, 45).—Three experiments were made on rabbits; 1 gram of strontium bromide was given by the œsophagus daily. Death occurs more rapidly than with potassium bromide. The following numbers represent the daily amount given per kilo. of body weight, and that recovered in the tissues after death:—

	Dose.	Recovered.
1.....	4 doses of 0·59	1·715 per kilo.
2.....	9 doses of 0·76	2·121 „
3.....	10 doses of 0·438	1·57 „

Accumulation thus occurs much in the same proportion as with potassium bromide.

W. D. H.

Accumulation of Potassium Bromide in the Organism. By C. FÉRÉ and L. HERBERT (*Compt. rend. Soc. Biol.*, 1892, 130—132).—In two epileptics, who had for lengthy periods been treated with potassium bromide, *post-mortem* analysis indicated a predominance of accumulation of the drug in the cerebellum as compared with other parts of the nervous centres, but the greatest accumulation was in the nerves and liver.

W. D. H.

Localisation of Mercury in the Animal Organism. By ULLMANN (*Chem. Centr.*, 1892, ii, 941; from *Pharm. Post*, 25, 1099—1101).—The author employed Ludwig's method (this vol., ii, 243) for the detection of the mercury. The distribution of the mercury in the organism always follows the same laws whatever the dose or the form of administration. The largest amount of mercury is found in the kidneys, liver, and spleen, in the order given. As regards the

digestive tract, the stomach contains very small but weighable quantities, whilst more is found in the small intestine, and still more in the large intestine. Small weighable quantities are found in the heart and skeletal muscles and in individual cases, also in the lungs. The brain, salivary glands, abdominal gland, thyroid gland, bile, and bone substance contain unweighable traces, or, with small doses, not even a trace of mercury. A. J. G.

Keratohyalin. By P. ERNST (*Virchow's Archiv*, 130, 279—296).—This paper is chiefly histological. It discusses the question of what keratohyalin is. This name was given by Waldeyer to the substance in the cells of the *stratum granulosum* of the epidermis. It stains very differently to eleidin, the substance in the *stratum lucidum*. Eleidin, however, is not fat as some have considered.

The proposition is advanced that keratohyalin is nucleïn, or, at least, a derivative of nucleïn. It is certainly not keratin, nor is it hyalin. W. D. H.

Hyalin and Colloïd. By P. ERNST (*Virchow's Archiv*, 130, 377—417).—By the use of aniline and other dyes, microchemical differences can be shown to exist between the various substances included under the names hyalin and colloïd; and these are again different from mucin.

There appear to be two varieties of hyalin in hyaline degeneration (for instance, of muscle); one is derived from epithelial cells, being a degeneration or secretion product. In this category is included the colloïd of the thyroid, many colloïd renal casts, and the ovarian colloïd. The other variety arises from the connective tissues and the vascular apparatus; it is stained reddish-purple by acid solutions of magenta. To this category belong the hyaline degeneration of the interfollicular tissue of the thyroid, the hyaline residue of the *theka follicularis* of the ovary, and the more or less hyaline glomeruli of the kidneys and the hyaline network of tumours. W. D. H.

Alkalinity of the Blood during Muscular Work. By W. COHNSTEIN (*Virchow's Archiv*, 130, 332—360).—The following are the conclusions drawn from the experiments described:—

1. The alkalinity of the blood, both in carnivora and herbivora, decreases during muscular work.

2. The decrease goes on in herbivora *pari passu* with the work. In carnivora a minimum is soon reached, a regulating mechanism being apparently called into play to inhibit further lowering of the alkalinity.

3. The diet has considerable influence on the alkalinity of the blood in resting and working animals. By lessening the proteïd intake, carnivora are made similar to herbivora, in that the alkalinity of their blood undergoes more striking changes. W. D. H.

Glycogenic Function in Winter Frogs. By DEWEVRE (*Compt. rend. Soc. Biol.*, 1892, 19—21).—Contradictory statements as to the liver glycogen in frogs may be reconciled by considering the time of

year at which the observation is made. At the end of the hibernial period, there is no glycogen in the liver and no sugar in the blood. At the beginning, there is glycogen in the liver and sugar in the blood. Ablation of the liver in such animals does not cause the complete disappearance of sugar in the blood.

The rate at which the glycogen disappears from the liver varies in different frogs. It may be found absent after two weeks; in other cases 16 weeks may be necessary. The glycogen in the muscle increases as that in the liver goes, but in time the muscular glycogen is also used up.

All animals are not like the frog in these particulars: the marmot, for instance, becomes diabetic during hibernation. W. D. H.

Secretion of Hydrochloric acid in Nervous Dyspepsia. By R. GEIGEL and L. ABEND (*Virchow's Archiv*, 130, 1—28).—87 cases of nervous dyspepsia were examined: nothing characteristic in the gastric juice was found. On the average, however, the gastric juice was rather concentrated, as far as the acid was concerned. The absolute quantity of acid secreted was normal in 38, below the normal in 38, and above the normal in 11 analyses. W. D. H.

Lymph Secretion. By E. H. STARLING (*J. Physiol.*, 14, 131—153).—When “peptone” (that is, proteose *plus* peptone) is injected into the circulation of a living animal, it disappears gradually, and may still be found in the plasma one to two hours after the injection. The method used was to add to the blood or plasma an equal volume of trichloroacetic acid (10 per cent. solution). This reagent does not precipitate proteose or peptone, but completely precipitates the normal proteids of the blood.

The disappearance from the blood is caused in the first place by a transfer of “peptone” to the lymph, so that shortly after the injection the lymph contains more “peptone” than the blood plasma itself. This transference is effected by the selective activity of the cells of the vessel wall, and it is probable that a preponderating part is played by the endothelial cells of renal capillaries.

There is no connection between the loss of coagulability induced by the intra-vascular injection of “peptone” and the amount of peptone present in the plasma at any given time after injection.

W. D. H.

Transmission of Alcohol to Milk. By F. KLINGEMANN (*Exper. Stat. Record*, 4, 311; from *Molk. Zeit.*, 1892, No. 5).—Doses of alcohol (25 to 200 c.c.) strongly diluted were given to goats at night, and the milk of the following day examined. With 100 c.c. of alcohol, the next morning's milk contained 0.15 to 0.3 per cent. of alcohol, but the night's milk was free from alcohol. With 200 c.c. of alcohol, the yield of milk was reduced to about one-third and contained, in the morning 0.35 and in the evening 0.1 c.c. (? per cent.) of alcohol. No alcohol was found in human milk after the consumption of small quantities of alcohol, but with increased consumption small amounts were found.

N. H. M.

Milk of different Breeds of Cows. By P. COLLIER (*Exper. Stat. Record*, 4, 263—267; from *New York State Stat. Rep.*, 1891, 139—162).—The observations recorded were made with 15 cows, and extended over one (the first) period of lactation in each case. As regards composition, the constituent which showed least variation was the ash, the highest percentage being 0.760 (Devon), and the lowest 0.698 (Ayrshire and American Holderness). Fat is the most variable—from 3.46 (Holstein-Friesian) to 5.61 (Jersey) per cent. Casein varied from 3.39 (Holstein and Holderness) to 3.91 (Jersey); sugar from 4.84 (Holstein) to 5.33 (Ayrshire).

The microscopic examination of the milk of the 15 cows of the six breeds included the actual counting and measurement of 44,836 globules. The results showed that with the advance of the period of lactation, the relative number of the smaller globules increases with considerable regularity. A table is given showing the percentage of the fat in different sized globules; the results are important as bearing on the behaviour of the milks in butter and cheese making.

N. H. M.

The Acids of Ox Gall. By LASSAR-COHN (*Ber.*, 26, 146—151).—It has been previously shown (*Abstr.*, 1892, 1114) that myristic, palmitic, stearic, and oleic acids occur in ox gall, and can be separated in the form of their barium salts from a solution prepared in a suitable manner; when these barium salts are converted into sodium salts, the solution of the latter again treated with barium chloride, and the filtrate fractionally precipitated with hydrochloric acid, a brownish resin is obtained. This resin, on recrystallisation from glacial acetic acid, yields a colourless, crystalline acid, which has the composition $C_{24}H_{40}O_4$, and is identical with Latschinoff's choleic acid, and with Mylius' deoxycholic acid; on oxidation with chromic acid, the crystalline acid is converted into dehydrocholeic acid, $C_{24}H_{38}O_4$, identical with the compound described by Latschinoff. The quantity of choleic acid obtained by the author amounted to only 0.085 per cent. of the bile employed, whereas Latschinoff, who used bile from St. Petersburg, found about 1.6 per cent.; this, therefore, is the second case in which a difference of composition in samples of bile of different origin has been established, Emich having already drawn attention to the variation in the quantity of glycocholic acid.

The mother liquors from the choleic acid, obtained in the manner described above, contain cholic acid, the presence of which is due to imperfect washing of the precipitate of barium salts, and resinous acids.

For the estimation of cholic acid in bile the following process may be adopted:—The bile, 20 c.c., is mixed with sodium hydroxide, 2 grams, the solution boiled for 24 hours, and, after having been treated with carbonic anhydride, evaporated to dryness on the water-bath; the residue is extracted with boiling 96 per cent. alcohol, until free from the salts of organic acids which are only sparingly soluble in water, and the extract, after having been diluted with 4 vols. of water, is precipitated with a dilute solution of barium chloride, 0.5 gram. The filtrate is then acidified with hydrochloric acid, and the cholic acid extracted by shaking with ether, into which it readily

passes, because of the alcohol present; the alcoholic, ethereal solution is evaporated, and the residual cholic acid dried until constant.

A sample of fresh bile analysed in this way on November 20 was found to contain 4·86 per cent. of cholic acid; two other samples, examined a few days later, contained 4·68 and 4·69 per cent. respectively.

The percentage of the various acids present in bile which has been boiled with soda is as follows:—

Cholic acid....	4·790	Stearic acid	} 0·146
Choleic acid...	0·085	Palmitic acid ...	
Myristic acid..	0·004	Oleic acid	
Resinous acids	0·120	Loss	0·050

F. S. K.

Carbonated Albuminuria. By J. GAUBE (*Compt. rend. Soc. Biol.*, 1892, 399—402).—The author has previously stated that the albumin in urine is combined with calcium as an albuminophosphate. He now introduces the term carbonated albuminuria, to indicate the excretion by the kidneys of small quantities of albumin combined with alkali carbonates.

W. D. H.

Chemical Stimulation of Nerves. By E. W. GROVES (*J. Physiol.*, 14, 221—232).—The central portions of motor nerves (for instance, sciatic of frog) are much less irritable than the peripheral to chemical stimuli, though they are sooner killed by their action.

The irregularity, both in manner and extent, of the muscular response to a chemical stimulus stands in marked contrast to the exceedingly regular response to electrical stimuli.

Afferent nerves (for instance, vagus of rabbit) are almost unaffected by chemical stimuli.

W. D. H.

Action of Inorganic Salts on the Heart. By W. H. HOWELL, Miss E. COOKE, and R. G. EATON (*J. Physiol.*, 14, 198—220).—Paraglobulin was prepared by the magnesium sulphate and carbonic acid methods; it was dissolved, and the solution used as an artificial circulation through the frog's heart. The heart, however, could not be made to beat well. Serum, with all its constituents untouched, is an excellent circulating fluid. There is, however, no loss in its proteid contents after it has been passed through the heart. Serum decalcified by admixture with sodium oxalate, is also inefficacious in keeping the heart beating.

Ringer's fluid is a mixture containing no proteids, but simply inorganic salts, approximately the same in amount and proportion as in blood. It keeps the heart going well; in one experiment here recorded for 30 hours. The heart had been thoroughly washed out with normal salt solution before the experiment, so there could have been little possibility of any blood being retained by the heart. An aqueous extract of serum (which had previously been dried and heated to coagulate proteid matter) acts even better than Ringer's fluid, and the inorganic salts of milk, similarly obtained, act in the same way.

The saline matter in saliva, and saliva itself, will not maintain the heart's activity, but the salts obtained from the gastric secretion will do so. Kronecker and his pupils (Abstr., 1889, 632) have stated that serum albumin is the only substance that will maintain the heart's activity. They find that peptone will not do so, until it has been placed in contact with the gastric mucous membrane; the action of the epithelial cells is stated to be to regenerate albumin from the peptone. There is no chemical proof of this, but the fact that the mixture now keeps a heart beating is regarded as sufficient proof of the regeneration of albumin. The fallacy in reasoning here is obvious. These experiments, moreover, show that it is probably the admixture with the inorganic salts which gave the "peptone" power to keep a heart going. Some recent experiments with gum arabic (Heffter, *Arch. exper. Path. Pharm.*, 29, 41) are to be explained also on the presence of calcium and potassium salts mixed with the arabin.

The most probable explanation of the way that inorganic salts act, is that they serve as chemical stimuli of the heart muscle.

W. D. H.

Physiological Action of Iodine Compounds. By L. LAPICQUE (*Compt. rend. Soc. Biol.*, 1892, 108—119).—Various iodine compounds doubtless owe their activity to the iodine they contain. The proof of free iodine in the body, after their administration, has never been given. In the present experiments, various compounds of iodine were injected into the vessels, and the time of onset and intensity of the symptoms noted. It was found that the toxic action of the injected material varies as one would expect from chemical considerations, based on the hypothesis that a decomposition of the compound occurs in the organism. The least stable compounds produce their effects most readily.

W. D. H.

Action of Strontium Iodide on the Circulation. By L. LAPICQUE and A. MALBEC (*Compt. rend. Soc. Biol.*, 1892, 499—500).—The first effect noticed is a slowing of the heart and a rise of blood pressure, followed by the opposite, and is thus very similar to that observed with potassium iodide. The primary effect is due to the strontium, not the iodine.

W. D. H.

Action of Iodides. By L. LAPICQUE (*Compt. rend. Soc. Biol.*, 1892, 536—540).—The main effect of the iodides is a lowering of arterial tension and acceleration of the heart. In producing this effect, iodides of calcium and potassium act with the smallest dose, then follow in order those of strontium and sodium.

The action appears to be independent of the medullary centres.

W. D. H.

Physiological Action of Chloralce. By HANRIOT and C. RICHET (*Compt. rend.*, 116, 63—65).—See this vol. i, 247.

Physiological Action of Atropine and Pilcarpine. By J. P. MORAT and M. DOYON (*Compt. rend. Soc. Biol.*, 1892, 707—710).—These two drugs act in an inverse way on the respiratory movements;

atropine accelerates, and pilocarpine slows them. They antagonise one another when administered successively.

W. D. H.

Physiological Action of Cinchonamine Sulphate. By ARNAUD and CHARRIN (*Compt. rend. Soc. Biol.*, 1892, 671—672).—Cinchonamine, $C_{19}H_{21}N_2$, obtained from the *Remijia Purdieana*, is poisonous; its sulphate provoking tonic convulsions. Like quinine, it is a febrifuge.

W. D. H.

Physiological Action of Cupreïne and its Derivatives. By E. GRIMAUX and J. V. LABORDE (*Compt. rend. Soc. Biol.*, 1892, 608—613).—The physiological effects of these substances present great resemblances, differing in the degree of activity according to an ascending scale from cupreïne to quinopropylene. Quinine in the normal state is not antithermic, whilst these substances are. Not only is there lowering of temperature, but also stupefying and analgesic effects.

W. D. H.

Toxic Action of Expired Air. By J. HALDANE and J. L. SMITH (*Journ. Pathol. and Bacteriol.*, 1, 318—321).—Further experiments performed on Merkel's plan (*Arch. Hygiene*, 15, 1) lend no support to Brown Séquard's hypothesis (supported by Merkel) that expired air contains a special organic poison. The results obtained confirm those previously published by the authors (*Abstr.*, 1892, 1502).

W. D. H.

Antiseptic Treatment of Wounds. By E. P. NILES (*Exper. Stat. Record*, 4, 360; from *Virg. Stat. Bul.*, No. 18, 1892).—Lysol (2 per cent.) prevented the growth of micro-organisms and decreased the amount of suppuration when used for washing a wound on a horse. Creolin (1 per cent.) retarded the growth of pus-producing organisms, but did not destroy them in 15 minutes. Dermatole, iodole, aristole, zinc oxide, and mercuric chloride were found to be unsuitable. Mercuric chloride (1 : 1000) retarded the growth of organisms, but was not strong enough to be of use, whilst stronger solutions are injurious to the tissues.

N. H. M.

Chemistry of Vegetable Physiology and Agriculture.

Bacteria of the Stomach. By A. L. GILLESPIE (*Journ. Pathol. and Bacteriol.*, 1, 279—302).—Many organisms grow in the stomach even when its contents are acid. When organic acids are present, bacteria can be grown which produce the same acids in suitable media. Proteid hydrochlorides have very little inhibitory power on organisms as compared with free hydrochloric acid. Excess of bacterial growth is deleterious to gastric and pancreatic digestion; the presence of bacteria fulfils a useful purpose in the intestine, the acids they produce controlling putrefaction. The formation of leucine and tyrosine does not seem to be aided by the presence of bacteria.

W. D. H.

Liberation of Nitrogen during Putrefaction. By H. B. GIBSON (*Amer. Chem. J.*, 12—18).—Lean beef or blood serum covered with water was allowed to putrefy in a confined atmosphere, which was renewed from time to time by admitting purified air. The nitrogen was determined in a sample of the material at the beginning of the operations, water and either emulsion of putrid meat or soil infusion was then added to a known amount of material, and putrefaction allowed to proceed at the ordinary temperature for periods varying from 63 to 168 days. The volatile nitrogenous products of putrefaction, such as ammonia, indole, and skatole, were removed from the discarded air by sulphuric acid. At the end of the operations, the nitrogen was estimated in the whole of the putrefied material by the Kjeldahl process, and the loss, due allowance having been made for the volatile nitrogenous substances, calculated as nitrogen liberated during the experiment.

With putrid meat emulsion, the loss was small, ranging between 1 and 4·4 per cent., but with soil infusion it rose to 9·6—15 per cent. Nitrates and nitrites were not present at any stage of the operations, and hence, when putrefaction is started by means of soil infusion, there seems to be extensive direct conversion of organic into free nitrogen. JN. W.

Soluble Pentoses in Plants. By G. DE CHALMOT (*Amer. Chem. J.*, 15, 21—38).—See this vol., i, 247.

Production of Albumin in Plants. Co-operation of Phosphoric acid. By A. MAYER (*Landw. Versuchs-Stat.*, 41, 433—441).—Whilst it is maintained that phosphoric acid is necessary for albumin formation, manuring experiments show that nitrogenous matter applied alone induces much growth, and this can only be due to the organised nitrogen, inasmuch as the most important vegetative phenomena proceed from the highly nitrogenous protoplasm. In order to obtain some explanation of this, winter rye was grown in soil (very exhausted as regards phosphates) and manured with nitrate and with kainite and superphosphate respectively. The rye receiving nitrate grew far more luxuriantly than the other. As was shown long ago by Arendt (with oats), the plants contained much more proteids and ash in the early stages of growth than at subsequent periods. A more important point, as bearing more directly on the object of these experiments, was the fact that the percentage of pure protein in the crude protein was practically the same (about 70 per cent.) in the produce of both plots. Similar results were obtained with grass. The production of proteids is thus very rapid, and intermediate products, as amides, do not exist for any length of time. As regards the amount of phosphoric acid in the plants of the two plots, there was no considerable difference. The soil, although much exhausted, contained too much phosphoric acid for the experiment. Accordingly, an infertile, siliceous, diluvial sand was next employed, manured on the one hand with sodium nitrate, gypsum, and kainite, and on the other with superphosphate and kainite. The plants (again rye) did not grow luxuriantly and the nitrate vessels did not pro-

duce much more than the others. The ears in Experiment 1 (nitrate) were larger than those in Experiment 3 (phosphate), but there were 3 more in No. 3. The results showed clearly that nitrate produces less, or at any rate not more, nitrogenous matter when phosphates are absolutely wanting. The absence of phosphates (and of nitrogen) gives rise to limited growth, and not to a growth of different composition, so that the forcing action of the nitrates hardly comes in.

The chief reason against heavy nitrogen manuring is not the waste of the most costly manure with insufficient representation of other manures, but the fear of injuring the crop, either through its becoming too bulky, in consequence of which the plants shade each other (hindering the production of carbohydrates), or by prolonging the development of the plants, thus delaying ripening.

The results of the above experiments do not dispose of the question of a connection between proteids and a single ash constituent, phosphoric acid.

N. H. M.

Composition and Nutritive Value of the Tubers of *Stachys tuberosa*. By F. STROHMER and A. STIFT (*Bied. Centr.*, 21, 820—822; from *Oest. ungar. Zeits. Zuckerind. u. Landw.*, 1891, 1—4).—The tubers contained 21·95 per cent. of dry matter. The percentage composition of the dry substance, freed from sand, was found to be as follows:—

Albumin.	Non-proteids.	Crude fat.	Crude fibre.	Crude Stachyose.	Pure ash.	Not determined.	K ₂ O.	P ₂ O ₅ .
5·34	14·33	0·73	3·33	63·50	5·48	7·20	2·62	1·00

The following numbers show the percentage amounts of nitrogen in various forms:—

Albumin.	Nuclein.	Ammonia.	Amido-acid amides.	Amido-acids.	Not determined.
19·01	8·13	7·81	42·96	16·26	5·80

The nutritive value of the tubers resembles generally that of vegetables and potatoes, but they are more digestible and contain more nitrogenous nutritive matter (compare v. Planta, *Abstr.*, 1890, 1183).

N. H. M.

Composition of the Stems and Leaves of Tomatoes. Presence of Boron, Lithium, and Copper in the Plant. By N. PASSERINI *Staz. Sper. Agrar.*, 20, 471—476).—The author has already investigated the composition of the fruit of tomatoes (*Abstr.*, 1891, 256). As regards the stems and leaves, the fresh stems contained 8·84—9·92 per cent. of dry matter, and 1·57—1·96 per cent. of crude ash; the fresh leaves contained 11·62—14·62 per cent. of dry matter, and 1·60—3·23 per cent. of crude ash. The dried stems and leaves contained respectively 1·8995 and 1·4374 per cent. of nitrogen. The percentage composition of the pure ash of (I) the stems and (II) the leaves was found to be as follows:—

	K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	Mn ₂ O ₄ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
I.	24·95	11·08	32·80	7·87	0·84	—	2·29	4·69	6·05	14·48
II.	1·95	1·37	38·14	9·00	0·14	0·05	1·36	12·79	33·84	1·83

A good crop (50,000 kilos. of fresh fruit per hectare), excluding the leaves, which are usually returned to the soil, would take from the soil: nitrogen, 113·7 kilos.; phosphoric anhydride, 50·7 kilos.; potash, 256·6 kilos.; lime, 58·4 kilos.; and magnesia, 23·8 kilos.

An aqueous extract of the ash of the stems, from which sodium and potassium had been separated, was examined spectroscopically, when the lithium line α was distinctly seen. Another portion of the extract was found to contain boron (Rose's method). The insoluble portion of the ash contained copper in quantity sufficient to be detected by means of ordinary reagents. In connection with this, it is mentioned that the plants analysed were grown in the open country, and that no copper preparation had been used for destroying injurious insects; in the analytical processes, the use of copper vessels was avoided. Barium and strontium could not be detected.

N. H. M.

Composition of Chick-Peas (*Cicer arietinum*). Presence of Boron, Lithium, and Copper in the Plant. By N. PASSERINI (*Staz. Sper. Agrar.*, 21, 20—30).—The only analyses of chick-peas hitherto published seem to be those of Berthier (*Selmi's Enciclop. Chim.*, 4, 449) and Ritter (*Bied. Centr.*, 1884, 529). The fresh substance of the stems, leaves, and the entire pods contains 27·54, 24·39, and 19·85 per cent. of dry matter (at 105°); in the dry matter of the various parts of the plant the following amounts of crude ash were found:—Stems, 10·44; leaves, 11·91; husks, 6·73; pods, 3·47. The dry matter of the seeds, amounting to 85·81 per cent. of the fresh substance, has the following percentage composition:—

Nitrogenous matter.	Fat.	Amides.	Sugar.	Cellulose.	Pure ash.	Nitrogen.
26·19	5·23	52·50	3·65	1·71	3·29	4·19

The seeds are thus particularly rich in nitrogenous matter, which represents more than a quarter of the whole. Seeds of beans and white kidney beans were found to contain 20·46 and 19·46 per cent. of nitrogenous matter respectively. The amount of amides in the seeds of chick-peas is also very remarkable.

The dry matter of (I) the stems, and (II) the leaves of chick-peas has the composition

Nitrogenous matter.	Fat.	Cellulose.	Other carbohydrates.	Pure ash.	Nitrogen.
I. 6·35	1·83	34·96	49·05	7·81	1·02
II. 14·21	4·11	13·93	58·92	8·83	2·27

The percentage composition of the ash of (1) the seeds, (2) stems, and (3) leaves is given next.

	K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	Mn ₃ O ₄ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
1.	24·60	1·29	4·45	19·98	2·42	—	39·56	3·38	0·71	2·85
2.	48·38	0·45	23·55	4·38	2·14	0·03	5·29	5·79	6·21	3·78
3.	29·58	0·86	40·63	3·33	3·01	—	5·96	4·43	11·30	1·86

As in the case of other *Leguminosæ*, the percentage of potash in the

straw ash is very high; in fact, nearly half the total ash. The calcium is chiefly accumulated in the leaves, and the magnesium in the seeds. With regard to the more important constituents, a good crop of 80 kilos. of seeds and 2000 kilos. of straw per hectare would remove: nitrogen, 52·8 kilos.; phosphoric anhydride, 18·1 kilos.; potash, 74·6 kilos.; calcium, 34·3 kilos.; and magnesium, 11·5 kilos.

The examination for rare elements was carried out as already indicated (preceding abstract). The presence of boron was clearly shown; lithium was detected by means of the spectroscope, and copper was found in the pure ash of the stems to the extent of 0·082 per cent. This result, however, notwithstanding the care taken, is given with some reserve, as it seems rather high. N. H. M.

Composition of *Iris germanica*. Presence of Boron, Lithium, and Copper. By N. PASSERINI (*Staz. Sper. Agrar.*, 21, 565—573).—The rhizomes, leaves, and flowers of *Iris germanica* contained in their natural state 42·19, 18·15, and 8·51 per cent. respectively of dry matter, and 1·34, 2·84, and 0·86 per cent. of crude ash. The following numbers show the percentage composition (I) of the dried rhizomes, and (II) of the dried leaves:—

Nitrogenous						Not	Pure
Nitrogen.	matter.	Fat.	Cellulose.	Amides.	Glucose.	determined.	ash.
I. 1·39	8·68	9·62	4·66	57·04	6·72	9·62	5·64
II. 0·77	4·83	2·24	23·56	59·50			9·87

The fatty matter when heated at 100° gives off a pungent, irritating vapour. The pure ash of (1) the rhizomes and (2) the leaves has the following percentage composition:—

	K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	Mn ₃ O ₄ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
1.	33·18	1·71	41·06	3·25	2·71	0·02	8·11	3·85	5·24	1·83
2.	37·18	1·05	42·74	2·92	0·49	0·03	7·28	3·40	1·47	1·93

Notwithstanding the high percentage of lime found in the ash, the plant is known to grow luxuriantly in soil containing only 0·85 per cent. of lime.

Boron and lithium were found in the ash of the leaves, and 0·022 per cent. of copper in the pure ash of the rhizomes. N. H. M.

Analyses of Oranges. By J. M. PICKELL and J. J. EARLE (*Exper. Stat. Rec.*, 4, 346—348; from *Florida Stat. Bul.*, No. 17, 1892).—The average percentage composition of a large number of different kinds of oranges was found to be as follows:—

Dry matter.		Nitrogen.		Organic matter.					
12·29		0·124		11·24					
SiO ₂ .	SO ₃ .	P ₂ O ₅ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	Cl.	
0·010	0·042	0·077	0·006	0·207	0·045	0·479	0·039	0·011	

Different oranges of the same species differ sometimes very con-

siderably as regards ash constituents, the difference being due to variations in soil and climate.

N. H. M.

Experiments with Wheat on the Substitution of Beryllium for Magnesium. By F. SESTINI (*Staz. Sper. Agrar.*, 20, 256—258; compare *ibid.*, 15, 290—298).—The experiments now described were similar to the earlier ones (*loc. cit.*), except that a white quartz sand was employed which had been previously boiled with hydrochloric acid. They were commenced the middle of February; there were two pots, each with ten seeds, but only three germinated, and at the end of May five more seeds were sown in each pot; four of them germinated. The plants were watered alternately with the nutritive solution containing beryllium and with distilled water. The growth was at first very slight, and the leaves very narrow. By the 15th June, four plants were 0·4 metre high, and on the 22nd one plant (0·52 metre high) began to form ear. Altogether six plants developed ears, one of which contained 8, another 5, and a third 1 grain, the rest being empty. The average weight of the grains was 0·026 gram.

The results of the experiments indicate that, whilst beryllium may take the place of magnesium in the growth of wheat, it is not a complete substitute for magnesium in the production of seed; under these circumstances, seed production becomes difficult, and the seed which is formed is little disposed to germinate.

N. H. M.

Loss of Nitrogen in Manures. By A. MUNTZ and A. C. GIRARD (*Compt. rend.*, 116, 108—111).—The authors have shown (this vol., ii, 181) that very serious loss of nitrogen takes place in the stables, &c., before the manure is put into heaps. Direct experiment shows that this loss is considerably reduced if an equal weight of peat is substituted for the ordinary straw litter. In a stable with 16 horses, the loss of nitrogen was 63·6 per cent. of that consumed when a straw litter was used, and only 48·3 with a peat litter. The loss is also less if dry earth rich in humic substances is used; in a sheepfold with 25 sheep, the loss was 50·2 per cent. with straw litter, and 25·7 per cent. with earth litter. The good effect of the earth depends on the quantity of humus that it contains. Direct experiments showed that the addition of small quantities of iron sulphate or calcium sulphate to the straw litter was practically without effect on the loss of nitrogen. A not inconsiderable proportion of the alkaline bases in the manure are non-volatile; the weight of sulphuric anhydride (SO_3), saturated by the non-volatile alkaline bases in 1 kilo. of manure, is as follows:—Horses, 1·352 gram; cows and oxen, 3·646 grams; sheep, 4·290 grams; pigs, 2·022 grams.

Taking into consideration the cost of material and subsequent treatment, it would seem that where peat is not readily accessible, the most useful plan would be to sprinkle earth, as rich in humus as possible, over the usual straw litter.

C. H. B.

Effect of Phosphate-manuring on the Amount of Sugar, and the Value of Beet-root. By M. MAERCKER (*Bied. Centr.*, 21, 804—808; from *Der Landwirth*, 1892, Nos. 66, 67, and 68).—Experi-

ments were made in which beet-root was grown in soil manured with 36—40 lbs. of phosphoric acid per morgen (63—70 lbs. per acre), with 14—18 lbs. per morgen (25—32 lbs. per acre), and without the application of phosphates. The soil was a normal beet-root soil—a mild loam generally over marl. The results, as regards sugar, gave practically no difference in favour of phosphoric acid. There was also no great difference in the yield of roots, although, the year (1891) being exceptionally favourable, a correspondingly large amount of phosphates would be required.

The mechanical properties of soil seem undoubtedly to be improved by phosphatic manuring, but this should be effected in a less costly manner. The results indicate that the large amounts of phosphoric acid sometimes applied (as much as 140 lbs. per acre being sometimes given) are excessive.

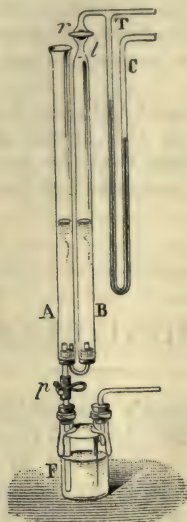
N. H. M.

Analytical Chemistry.

New Accessory to Lunge's Gas-volumeter. By J. A. MULLER (*Ann. Chim. Phys.* [6], 24, 570—574).—When it is required to measure the air or nitrogen displaced by a gas or vapour, as in the determination of vapour density by V. Meyer's method, or the volumetric estimation of carbonic anhydride in carbonates by Scheibler's process, and in all cases where the volume of the generating vessel is very great as compared with that of the gas to be measured, the displaced gas cannot be collected over mercury on account of the high specific gravity of the latter, but must first be collected over water. It is pointed out, however, that the volume of the displaced gas often differs, by reason of variations of temperature and pressure during the experiment, from that of the vapour or gas generated. For example, during the decomposition of a mixture of alkali carbonate and hydroxide by hydrochloric acid heat is developed, and it is necessary to wait about an hour for the reaction flask to attain an equilibrium of temperature. If now the surrounding temperature and pressure have varied in an opposite direction, the volume of the collected gas may vary from that of the liberated carbonic anhydride. To obviate this cause of error, there is placed by the side of the generating apparatus a vessel of like capacity full of air; the difference between the pressure of this air and that of the atmosphere is indicated by a water manometer. The arrangement shown in part below permits this difference to be determined, so that the error it gives rise to can be eliminated by increasing or diminishing the pressure at the end of the experiment.

A and B are two glass tubes of about 2 cm. diameter and 40 cm. in length; they are in communication at the lower ends. The manometer, attached to T, is half filled with coloured water. A and B are filled with water by opening the tap *t* and the pinchcock *p*, and compressing the superincumbent air in F by a caoutchouc bladder; when

the generating apparatus and the vessel containing air (mentioned above) have attained a constant temperature, they are connected with the tubes T and C respectively. The gas to be measured is then

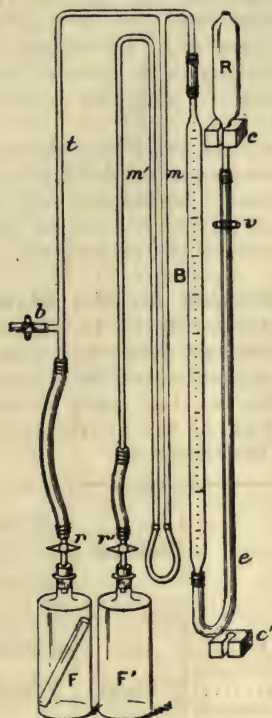


passed into the tube B, and the water allowed to flow out at the same rate by opening *p*. If the indication of the manometer C is not the same at the termination of the experiment as at the commencement, the equilibrium is restored by raising or depressing the level of the water in A. After this, the tap *r* is closed, the generating apparatus and the other vessel disconnected from T and C, and the gas passed into a Lunge's gas-volumeter at a constant temperature to be measured.

A. R. L.

New Gas-volumeter. By J. A. MULLER (*Bull. Soc. Chim.* [3], 7, 507—511).—The apparatus figured below serves for the measurement of gases evolved by reactions which take place at the ordinary temperature. It is composed of two vessels, F and F', having each a capacity of 500 c.c.; they are fitted with singly bored india-rubber stoppers through which pass tubes fitted with taps *r* and *r'*. F communicates with the burette by the tube *t*. The upper portion of *t* is attached to one of the branches of the water manometer *m*, the other branch *m'* communicating with F'. The burette B has a capacity of 500 c.c., and is divided into tenths from the upper portion downwards. The lower portion of the burette is attached by a stout caoutchouc tube *e* to a reservoir R, holding 60—70 grams of mercury. The small tube *b* is furnished with a piece of caoutchouc tubing and a screw clamp. The whole apparatus is fixed in a small cupboard which is only opened to perform the necessary manipulations or readings. More-

over, in order to ensure that the two vessels F and F' are as near as possible of the same temperature, they are covered with a thick metal box which is readily taken to pieces.



The apparatus may have been thus left over night in a room in which the temperature has varied slightly, care having been taken to previously withdraw the plugs of the taps r and r' , and to raise the mercury to the zero point of the burette. On the day following, the plugs of the taps are replaced, and the air shut up in the apparatus at a known temperature and pressure. The volume of the latter at

0° and 760 mm. will, when it is dry, be $V = \frac{P}{760 \times (1 + \alpha t)}$, or, when it is moist, $V = \frac{P - f}{760 \times (1 + \alpha t)}$, f being the tension of aqueous vapour at t° , and α the coefficient of expansion of the gas.

F is now charged with the necessary reagents, the taps closed, and the reaction started by inclining F. When the reaction is complete, the mercury reservoir is lowered and suspended in the lower holder c' . The tap r is now slightly opened, the clamp v loosened, the operator being guided in this portion of the operation by the levels of the water in the manometer. When these levels are again at the same

height, the clamp *v* is tightened. The reaction flask is agitated, and the apparatus allowed to remain for several hours. The tap *r'* is then opened, and the mercury in the burette is caused to ascend or descend, so as to readjust the level of the water in the manometer. The volume of the gas is then read off. This value multiplied by *V* or *V'*, according to whether the gas is dry or moist, gives the volume of the gas under normal conditions; the weight of the gas is obtained by multiplying this volume by the weight of 1 c.c. of the dry gas.

In making a fresh experiment, if the surrounding temperature and pressure are not the same as in the determination of the constants *V* and *V'*, it will be necessary before starting the reaction to aspirate out or force in a small quantity of air to readjust the level of the water in the two branches of the manometer.

A. R. L.

Comparison of Methods for the Standardisation of Acid and Alkaline Solutions. By C. L. PARSONS (*J. Anal. Chem.*, **6**, 372—375).—The experiments were made with an approximately N/5 hydrochloric acid and approximately decinormal ammonia and barium hydroxide solutions, the two last being so made that 2 c.c. of either should exactly equal 1 c.c. of the hydrochloric acid. The following table is a summary of the results:—

Method.	Indicator.	Grams NH ₃ in 1 c.c. solution.	Grams HCl in 1 c.c. solution.	Grams Ba(OH) ₂ in 1 c.c. solution.
By precipitation as (NH ₄) ₂ PtCl ₆ ..	—	0·001545	0 006634	—
By neutralisation with potassium tetroxalate.....	litmus	0·001560	0·006698	—
By neutralisation with potassium hydrogen tartrate	litmus	0·001564	0·006716	—
By precipitation as AgCl	—	0·001558	0·006679	0·007822
By pure pulverised Iceland spar..	cochineal	0·001567	0·006728	0·007880
By distillation of NH ₃ from NH ₄ Cl	cochineal	0·001563	0·006717	0·007866
By precipitation as BaSO ₄	—	—	0·006676	0·007820
By neutralisation with potassium tetroxalate	phenolphthalein	—	0·006722	0·007875

It will be seen that in every case the figures obtained by gravimetric methods are lower than those obtained by volumetric methods. The estimations obtained by silver chloride and barium sulphate agree closely. Those by ammonium platinochloride are lower, as would be expected from the comparatively greater solubility of the salt. Taking convenience also into account, the silver chloride is undoubtedly the best of the gravimetric methods of standardisation. The author then discusses the volumetric methods, and concludes by saying: "The determinations made by the aid of potassium tetroxalate are almost exactly the average of all the results, both gravimetric and volumetric, and are, in my opinion, the most accurate."

A. J. G.

Potassium Tetroxalate for Akalimetry. By C. L. PARSONS (*J. Anal. Chem.*, 6, 375—380).—Many samples of commercial potassium tetroxalate prove, on examination, to be mixtures of the tetroxalate with varying quantities of potassium hydrogen oxalate; this fact probably explains why such varying opinions have been expressed as to the suitability of potassium tetroxalate as a standard for alkalimetric work. Pure potassium tetroxalate, $\text{KHC}_2\text{O}_4, \text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$, is prepared either from potassium carbonate and oxalic acid or from the commercial salt. Oxalic acid is added to a boiling solution of the salt, the heating continued for an hour, and the liquid allowed to cool, when the salt separates in well formed crystals, which are washed once by decantation with water, and recrystallised several times from pure distilled water. The crystals are then pressed between filter paper and dried for 12 hours over sulphuric acid. The salt thus obtained, although containing water of crystallisation, is perfectly stable in air.

For titration against solutions of the fixed alkalis, phenolphthalein is the best indicator; for ammonia solutions, litmus must be employed, the point taken being the distinct appearance of the blue colour, which is sharp and unmistakable.

A. J. G.

Employment of Borax for standardising Acids. By E. RIMBACH (*Ber.*, 26, 171).—The author recommends the employment of borax in place of sodium carbonate for standardising normal acids, methyl-orange being used as indicator, which, from the observations of Joly (*Abstr.*, 1885, 440) and the author, is shown to be unaffected by boric acid. The author's investigation of the atomic weight of boron (this vol., ii, 207) shows that the method gives accurate results, and the salt has the advantage over sodium carbonate that it is more readily obtained pure, and that, owing to its high molecular weight, errors in weighing only affect the results to one-fourth the extent they would with sodium carbonate. For ordinary purposes, it is sufficient to recrystallise commercial borax two or three times, and allow it to remain in the air for two or three days with frequent turning over. 1 gram of crystallised borax, weighed in the air with brass weights, is equivalent to 5.2391 c.c. of normal acid, or 1 litre of normal acid corresponds with 190.872 grams of crystallised borax weighed under similar conditions.

H. G. C.

Detection of Hydrogen Peroxide. By G. GRIGGI (*L'Orosi*, 1892, 295—296).—The rapid disappearance of the blue colour of the ethereal extract of an aqueous solution of chromic anhydride and hydrogen peroxide may be avoided by substituting amyl alcohol for the ether. On shaking the solution of chromic anhydride and hydrogen peroxide with an equal volume of amyl alcohol, the latter acquires a magnificent indigo colour, which retains its original intensity for six hours at 24°.

W. J. P.

Estimation of Chlorine in Wine. By A. SOLARO (*Staz. Sper. Agrar.*, 21, 154—162).—Comparative experiments on the estimation of chlorine in wine were made, using the methods of Tony-Garcin as

modified by Dujardin, Roos (*Staz. Sper. Agrar.*, **18**, 758), and of Sinibaldi and Combe (*ibid.*, **20**, 635). For the experiments, two samples of wine were employed: to one, 0·2 per cent. of pure sodium chloride was added; to the other, 0·1 per cent. Determinations of chlorine in the ash from 100 c.c. of wine gave the percentage results 0·2078 and 0·1064 respectively. Dujardin's method gave very high results. Roos' method gave much better results, but generally rather low. Sinibaldi and Combe's method gave results almost identical with those obtained by Roos' method. Very good results are obtained as follows:—The wine is decolorised with animal charcoal, and 20 c.c. of the filtered liquid poured into a 50 c.c. flask, treated with a few drops of nitric acid, and an excess of N/20 silver solution; the volume is then made up to 50 c.c., and the whole shaken and filtered; to 25 c.c. of the solution, corresponding with 10 c.c. of wine, some more nitric acid and ammonium iron alum (0·5 c.c.) free from chlorides, are added; the excess of silver is then determined with N/20 ammonium thiocyanate; with wine No. 1, the highest and lowest results were respectively 0·2106 and 0·2061 per cent.; with No. 2, the results were 0·1199 and 0·1170 per cent. N. H. M.

Preparation of Standard Iodine Solution. By H. L. PAYNE (*Chem. News*, **66**, 286).—As a standard iodine solution alters on keeping for a long time, the author proposes a method whereby a litre of such a solution can be prepared in two minutes in any laboratory where a standard permanganate solution is constantly at hand. For this purpose, about 10 grams of potassium iodide is dissolved in a litre flask, and acidified with sulphuric acid; the calculated quantity of standard potassium permanganate is run in, and, after a few minutes, when the reaction is complete, the whole is diluted to the mark; a clear solution of known content of iodine is thus obtained, 5 atoms of iodine being liberated for each molecule of permanganate (KMnO_4).

D. A. L.

Estimation of Fluorine in the Ashes of Plants. By H. OST (*Ber.*, **26**, 151—154).—For the estimation of fluorine in vegetable ash, precipitation as calcium fluoride is out of the question, as it would be practically impossible to separate traces of calcium fluoride from such a complex mixture; under these circumstances the author employs the following method:—The ash from 15—20 grams of the air-dried substance is gently fused with silica ($1\frac{1}{2}$ parts) and fusion mixture (5 parts), the melt extracted with hot water, the filtered solution warmed with ammonium carbonate, kept for 12 hours, and again filtered to separate the silica, alumina, &c., the residue being washed with dilute ammonium carbonate. The solution is then evaporated until free from ammonia, almost neutralised with nitric acid, evaporated to dryness with a small quantity of a pure ammoniacal solution of zinc hydroxide, and the residue taken up with water; after filtering, the solution is again evaporated, the residue treated with water, the feebly alkaline filtrate, which is now free from ammonia and silica, heated to boiling, almost neutralised with nitric acid, and treated with calcium chloride. The precipitate is separated by filtration, evaporated with acetic acid in a platinum dish, and,

after completely expelling the acid, treated with water; the residue, which consists of calcium fluoride, calcium phosphate, and other substances, is placed in a platinum crucible, together with a few drops of sulphuric acid, the crucible covered with a weighed glass plate, and heated on a sand-bath, first at 100—150° for eight hours, and then more strongly, until sulphuric acid vapours begin to be evolved. The loss in weight of the glass cover is approximately proportional to the quantity of fluorine present, quantitative experiments with pure calcium fluoride having shown that 1 milligram of fluorine usually causes a loss in weight of 0·8 to 0·9 milligram.

Analyses of the ashes of the leaves of various plants, growing under healthy conditions, were made in this way, and in all cases a small quantity of fluorine (about 0·1 per cent.) was found; the results of quantitative experiments, in which a known weight of calcium fluoride was added to the plant ash before fusion, showed that 1 milligram of fluorine in the ash corresponds with a loss of about 0·5 to 0·6 milligram on etching.

F. S. K.

The Gunning-Kjeldahl Method, and a Modification applicable in the presence of Nitrites. By A. L. WINTON (*Exper. Stat. Record*, 4, 336; from *Conn. Stat. Bul.*, June, 1892).—The substance (0·5—1 gram) is digested for two hours with 30 c.c. of Sconell's salicylic acid mixture (sulphuric acid 30 c.c., salicylic acid 2 grams) in a 600 c.c. flask, being frequently shaken. Zinc-dust (2 grams) is gradually added, and the flask gradually heated to boiling. Potassium sulphate (12 grams) is now added, the boiling continued for a little while after the solution has become colourless (or is straw-coloured, as when iron is present). On cooling, as the whole begins to solidify, water is added, and the distillation with soda carried out in the usual manner. A table of results, obtained by the original method and by this modification, is given in the original paper. The greatest discrepancy is 0·1 per cent., and the average 0·05 per cent.

N. H. M.

Estimation of Phosphorus in Iron and Steel. By A. CARNOT (*Compt. rend.*, 116, 106—108).—About 5 grams of good iron or steel (or 0·5 to 1·0 gram if impure) is dissolved in 40 c.c. of pure nitric acid, and, when effervescence has ceased, the solution is gently heated, mixed gradually with 2 c.c. of concentrated sulphuric acid for each gram of metal, and evaporated gradually to dryness, with repeated stirring. The residue is heated at 120—125° for two hours in order to make the silica insoluble, dissolved in about 50 c.c. of boiling water, and the solution filtered. The residue, after treatment with hydrochloric acid to remove any manganese oxide, will give an accurate estimation of silicon, as in Drown and Shimer's method.

The filtered solution is heated to boiling for about half an hour with 1 gram of chromic acid, in order to oxidise the organic matter, and at the same time convert any pyrophosphoric acid into orthophosphoric acid; 60—80 c.c. of a 5 per cent. molybdc solution, prepared in the usual way, is then added, and the liquid is heated at 100° for two or three hours. After cooling, the clear liquid is decanted off, and the precipitate washed with tepid water containing

5 per cent. of the molybdic solution. The precipitate is then dissolved in 30 c.c. of ammonia solution, diluted with an equal volume of water, and poured through the filter on to which the washings had been decanted. If any insoluble matter remains on the filter, it is dissolved in warm, dilute nitric acid, and added to the acid solution which will presently be mentioned. The ammoniacal solution of the precipitate is cooled and gradually neutralised with nitric acid, care being taken that the temperature does not rise above 40° . As soon as a permanent precipitate separates, 3 c.c. more nitric acid is added, and the liquid is heated at about 40° for two hours. The precipitate is first washed with dilute nitric acid (1 : 100), and afterwards with water, and is dried at 100° and weighed. The weight of phosphorus contained in it is found by multiplying by 0.01628.

Analysis shows that the ammonium phosphomolybdate formed under these conditions has the composition MoO_3 , 90.720; P_2O_5 , 3.688; $(\text{NH}_4)_2\text{O}$, 4.160; H_2O , 1.432 = 100.000, which agrees almost exactly with the formula $\text{P}_2\text{O}_5, 24\text{MoO}_3, 3(\text{NH}_4)_2\text{O} + 3\text{H}_2\text{O}$.

C. H. B.

Estimation of Phosphoric acid as Magnesium Pyrophosphate. By H. NEUBAUER (*Zeit. anorg. Chem.*, 2, 45—50).—This method is not so trustworthy as is generally supposed. If the magnesium ammonium phosphate is precipitated in a solution containing free ammonia, together with more than a certain quantity of ammonium salts (as is the case when the phosphoric acid has been first precipitated as phosphomolybdate, then dissolved in ammonia, and reprecipitated with magnesia mixture) then the precipitate, when ignited, loses a small quantity of phosphoric acid. Probably some $\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2$ is precipitated along with the MgNH_4PO_4 , and when ignited loses, amongst other things, P_2O_5 , leaving $\text{Mg}_2\text{P}_2\text{O}_7$. That phosphoric acid is actually lost, was proved by covering the crucible with a lid coated with a thin layer of magnesium oxide; the lid increased in weight, and the coating could be shown to contain phosphoric acid at the end of the experiment.

Reasons are given for believing that a solution containing a known amount of phosphoric acid cannot accurately be made from either sodium phosphate or magnesium ammonium phosphate. The use of silver phosphate for this purpose is recommended. It is prepared by precipitation, purified by dissolving it in dilute nitric acid and reprecipitating with ammonia, gently ignited, and weighed. It is now dissolved in dilute nitric acid (any residue being collected, weighed, and its weight deducted from that of the silver phosphate), the silver is precipitated with hydrochloric acid, the filtered solution concentrated to drive off nitric and hydrochloric acids, and the residue diluted with water, filtered, and made up to a known volume. The weight of phosphoric acid in this volume = weight of silver phosphate taken \times 0.1695.

C. F. B.

Precipitation of Phosphorus as Ammonium Phosphomolybdate in the presence of Arsenic. By H. C. BABBITT (*J. Anal. Chem.*, 6, 381).—The author has made experiments on the estimation of phosphorus in steel by precipitation as ammonium phosphomolybdate, and

finds that if the temperature of precipitation is kept at or below 25° the presence of arsenic has no influence on the accuracy of the phosphorus determinations, but at temperatures above 25° arsenic is precipitated in amounts that increase rapidly with the temperature.

A. J. G.

Citrate and Molybdate Methods for the Estimation of Soluble Phosphoric acid. By M. MAERCKER (*Landw. Versuchs-Stat.*, 41, 329—373).—The paper is a report on comparative experiments made by the two methods at various German experimental stations and by representatives of manure manufacturers. A solution containing a known amount of phosphates was made, and samples distributed for analysis. With a view to avoid errors, the amounts actually analysed were in each case weighed instead of measured. Tables of the results obtained at the various stations are given. The greatest deviation from the average (0.1639 gram, using 50 grams of solution) was 1.6 milligrams by the molybdate, and 1.7 milligrams by the citrate method; or, as 1 milligram corresponds with 0.1 per cent. of the superphosphate employed, the greatest deviation would be ± 0.16 and ± 0.17 per cent. respectively. The results obtained by the various analysts generally agreed very well, but, taking all together, the results are not considered quite satisfactory, and it was decided to repeat the experiment.

In one case, a difference was noticed in molybdate precipitates which had been left 12 and 24 hours respectively after the mixture of superphosphate and molybdate had been kept for nearly half an hour. In the first case (which gave an average result of 0.1266 gram $\text{Mg}_2\text{P}_2\text{O}_7$), the precipitate was pure white; in the second case (average result 0.1286 gram), the precipitate was grey-white or grey-blue. The lower results with the white precipitate were probably the best.

A solution of pure sodium phosphate was next made, and, after its strength had been determined by evaporating to dryness and also by precipitation with magnesia mixture (by both methods, 50 grams was found to contain 0.1676 gram of P_2O_5), 50 grams of a solution containing pure iron (2.94 grams), pure alumina (2.24 grams), and pure calcium carbonate (43.90 grams per litre, dissolved in nitric acid) was added to every litre of the phosphate solution. On analysis, an absolutely correct average result was obtained. The citrate method gave on the average 0.0007 gram too much, and the greatest difference between the two methods was 1.4 milligrams of phosphoric acid. The citrate method was, therefore, unhesitatingly declared to be trustworthy.

Direct Estimation of Nitrogen in Chili Saltpetre.—Comparative experiments were made with the Jodlbauer, aluminium, and zinc-iron (Kühn) methods. It was decided that all three methods (the aluminium method being modified) are good, but Kühn's method was recommended on account of the ease and quickness with which it is worked. The method is as follows:—The nitrate (10 grams) is dissolved in water (1 litre), and 50 c.c. of the filtered solution put with water (120 c.c.) and aqueous soda (1.3 sp. gr., 80 c.c.) in an Erlenmeyer flask of 750 c.c. capacity. Zinc-dust (5 grams) and powdered iron (*ferrum limatum pulv.*, 5 grams) are then added, the

flask connected with a condenser, and the whole left for one hour. About 100 c.c. is then quickly distilled off into acid. A sketch of the apparatus is given, by means of which six distillations can go on at once. The flasks are provided with suitable bulbs to prevent the splashing over of any soda. The condensing tubes are of tin. The ends of the condenser do not dip into the acid, but the receivers are provided with safety tubes containing acid (the same as that in the receivers), which is eventually washed back into the flasks.

Decomposition of Basic Slag by means of Hydrochloric acid and of Sulphuric acid.—The results of several experiments in which hydrochloric acid and sulphuric acid respectively were used were decidedly against the use of the former acid, which, under some conditions, gives too high results. It was therefore decided to use sulphuric acid. The formation of crusts is avoided by adding a little sand to the acid; this causes the acid liquid to boil with more motion.

N. H. M.

Estimation of Phosphoric Anhydride in Basic Slag. By G. MANCUSO-LIMA (*Staz. Sper. Agrar.*, 21, 225—228).—The finely powdered slag (2 grams) is put into a flat dish and treated with sulphuric acid (25 c.c.) diluted with half its volume of water, stirring quickly with a glass rod; the pasty mass thus formed is left for about two hours, treated with warm water, filtered, and washed. Milk of lime free from phosphates is then added, the whole shaken, and, when alkaline, it is heated for about half an hour on a water bath, treated with nitric acid until the lime precipitate is redissolved, allowed to cool, and filtered. The solution is precipitated with ammonium molybdate, and the analysis continued in the usual manner. The method was compared with Olivieri's method, with that proposed by Martinotti, and with the Italian official method, a mixture of known composition, containing sodium phosphate (5 grams), iron (2 grams), manganese (2 grams), and potassium silicate (1 gram) being employed. With the exception of the official method, which gave results nearly 50 per cent. too low (owing to the formation of basic iron phosphate), the different methods gave fairly concordant results: Olivieri, 0.8605; Martinotti, 0.8948; and Mancuso, 0.830 gram. The actual amount was 0.835 gram. The three methods were then tried with the same slag, Martinotti's method being slightly modified in order to save time. Two grams of the slag was treated with 20 c.c. of strong hydrochloric acid and evaporated to dryness on a water bath; this operation was repeated, after which the residue was treated with fuming hydrochloric acid, dissolved in water, and made up to 100 c.c.; 50 c.c. of this was treated with ammonium citrate (120 c.c.) and ammonia (30 c.c.); 100 c.c. was then precipitated with magnesia mixture. The results were all very similar. The author prefers his method as being quicker.

N. H. M.

Estimation of Phosphoric Anhydride in Basic Slag. By D. MARTELLI (*Staz. Sper. Agrar.*, 21, 453—455).—The author has compared the methods of Martinotti (*Staz. Sper. Agrar.*, 19, 614), Olivieri (*ibid.*, 20, 159), and Mancuso-Lima (preceding abstract)

with that given by König in his *Untersuchung landw. und gewerbewichtiger Stoffe* (Berlin, 1891, pp. 178—179, and 163). He considers the methods described by König to be the best, as effecting a saving both of time and reagents.

N. H. M.

Eschka's Process for the Estimation of Sulphur. By F. HUNDESHAGEN (*Chem. Zeit.*, 16, 1070—1071).—Eschka has recommended igniting coal with a mixture of sodium carbonate and magnesium oxide, whereby the sulphur is converted into sodium sulphate. The author, however, has noticed that, even with the greatest care, there is an appreciable loss of sulphur, sometimes as much as 6 per cent. of the total amount. In fact, when analysing samples of coal rich in sulphur, part of this escapes as hydrogen or ammonium sulphide, easily detectible by lead paper.

If, however, potassium carbonate is used instead of the sodium compound, no loss of sulphur need be feared. The author now proposes the following plan:—A mixture is prepared, consisting of 2 parts of magnesium oxide and 1 part of calcined potassium carbonate. For 1 part of coal, 2 parts of this mixture are used, three-fourths of which is intimately mixed with the coal, whilst the remainder is sprinkled on the top. The operation seldom takes more than half an hour. The test analyses are satisfactory.

L. DE K.

Influence of the Sulphur contained in Coal Gas on the Estimation of Sulphur by Fusion. By J. D. VAN LEEUWEN (*Rec. Trav. Chim.*, 11, 103—105).—The best fusing mixture is stated to be that recommended by Böckmann, namely, potassium chlorate (1 part) and sodium carbonate (6 parts). The author's results confirm those obtained by others, that, by employing a coal-gas flame for the fusion, the percentages of sulphur found are too high.

A. R. L.

Gravimetric Estimation of Sulphuric acid. By M. RIPPER (*Zeit. anorg. Chem.*, 2, 36—44).—The usual method is vitiated by the fact that the precipitated barium sulphate carries down other matters, notably potassium salts, with it, and these are not readily removed by washing; and also by the fact that, when ignited with the filter paper, some of the sulphate is reduced to sulphide. When the total amount of sulphate is small, the consequent error may even reach 20 per cent. of the whole; if the modifications described below be adopted, it does not exceed 0·3 per cent. The washed precipitate is brought, whilst still moist on the filter, into a platinum crucible, and there burned. The ash is then treated with bromine water drop by drop, till the red colour of the bromine is permanent; by this means any sulphide that may have been formed is reconverted into sulphate. Another drop or two of bromine water and 10—15 c.c. water are now added, the whole is heated on the water-bath until the bromine has been driven off, 2—3 drops of hydrochloric acid are added, and the warming continued for 10 minutes. The precipitate in the crucible is now washed several times by decantation, the wash-water being poured off through a small filter; other substances carried down with the barium sulphate

are thus removed. The filter is placed in the crucible, the whole ignited, and the residue treated with a drop of bromine water, or of dilute sulphuric acid, again ignited, and weighed. C. F. B.

Volumetric Estimation of Sulphuric acid in Sulphates. By A. V. ASBÓTH (*Chem. Zeit.*, **16**, 922).—The author has tried the process recommended by Stolle (compare this vol., ii, 188), but has found that a solution of barium chromate in dilute hydrochloric acid does not keep, but rapidly decomposes, and will then, after addition of ammonia, contain barium chloride. Experimenting on pure potassium sulphate, using a barium chromate solution 24 hours old, the author only found 87 per cent. of K_2SO_4 ; and when using a five days old solution, the percentage fell to 55.1 per cent. With a freshly-prepared solution, good results may probably be obtained. L. DE K.

Estimation of Carbonic Anhydride in the Air of Buildings. By A. H. GILL (*Analyst*, **17**, 184—186).—The air to be tested is drawn into a bottle by means of bellows. The bottle, which should be perfectly clean and dry, should hold 4 or 8 litres, and be fitted with a rubber stopper carrying a glass tube closed by a small, unperforated rubber nipple. 50 c.c. of standard barium hydroxide is run in rapidly from a burette, the tip passing entirely through the tube in the stopper; the nipple is replaced and the solution spread completely over the sides of the bottle, while waiting three minutes for the draining of the burette before reading. The bottle is now placed upon its side, and shaken at intervals for 40—60 minutes. At the time when the baryta is added, the temperature and pressure should be noted. At the end of the above period, the bottle is well shaken, the cap is removed from the tube, and the bottle is quickly inverted over a 50 c.c. glass stoppered bottle, so that the solution shall come in contact with the air as little as possible. Without waiting for the bottle to drain, 15 or 25 c.c. of the baryta water is withdrawn with a pipette, and at once titrated with sulphuric (not oxalic) acid, using rosolic acid as indicator. The acid is made of such a strength that 1 c.c. equals 1 milligram of carbonic anhydride; therefore the difference in the number of c.c. of acid required to neutralise 50 c.c. of baryta water before and after absorption gives the number of milligrams of carbonic anhydride in the bottle.

In very correct analyses, notice should be taken of the amount of moisture present in the air. L. DE K.

Estimation of Rubidium by the Spectroscope. By F. A. GOOCH and J. I. PHINNEY (*Amer. J. Sci.*, **263**, 392—400).—Gooch and Hart (*Abstr.*, 1892, 913) have successfully estimated small quantities of potassium by means of the spectroscope. The authors have endeavoured to apply the idea to the estimation of rubidium. Sodium was, curiously enough, found to increase the brightness of the potassium line, and now it seems that it also remarkably increases the brightness of the rubidium line. Potassium has an effect similar to that of sodium. Too large proportions of either sodium or potass-

ium chloride are however injurious, but may be got rid of by precipitation with alcohol.

Whilst the estimation of potassium gave very satisfactory results, the errors introduced when estimating rubidium are manifestly large; but if the question is the estimation of only a few milligrams of the metal, the authors think that for want of a better process, the spectroscopic test may prove of some value. L. DE K.

Estimation of Calcium in Basic Slag. By A. F. HOLLEMAN (*Chem. Zeit.*, 16, 1471—1472).—The author has found that when estimating lime in a ferruginous substance, like basic slag, a combination of Classen's and Jones' methods should be employed. 50 c.c. of the solution, containing 1 gram of sample, is concentrated to a small bulk, and then mixed with 20 c.c. of a solution of potassium oxalate (1—3). After digesting on the water-bath for about 10 minutes, the calcium oxalate is collected, and washed with hot water until the washings are free from oxalate. The precipitate is now washed off the filter, and then dissolved in 15 c.c. of hydrochloric acid. To avoid loss, the filter must also be rinsed with a little weak acid. After evaporating down to 25 c.c., 10 c.c. of dilute sulphuric acid (1—5) is added, and then 150 c.c. of alcohol. After a few hours the calcium sulphate is collected on a filter and washed with alcohol until the washings give no colour with methyl-orange. The sulphate is then heated, with the usual precautions, to constant weight. The test analyses prove the remarkable accuracy of the process.

L. DE K.

Quantitative Separation of Strontium and Calcium Nitrates by means of Amyl Alcohol. By P. E. BROWNING (*Amer. J. Sci.*, 266, 462—463).—The author (compare Abstr., 1892, 916) recommended boiling about 0.5 gram of the mixed nitrates with two successive portions of 30 c.c. of amyl alcohol. He now states that 10 c.c. each time is quite sufficient, which lessens the allowance for the solubility of strontium nitrate.

L. DE K.

Quantitative Separation of Barium and Strontium by the action of Amyl Alcohol on their Bromides. By P. E. BROWNING (*Amer. J. Sci.*, 264, 459—462).—The author has found that 10 c.c. of amyl alcohol dissolves only an amount of barium bromide equivalent to 0.0013 gram of barium oxide; whilst, in the case of calcium, as much as 0.2 gram is dissolved. The author has founded on this fact an excellent method for separating the two metals, the *modus operandi* being very similar to the one previously described (compare Abstr., 1892, 915). After the bromides have been separated by the amyl alcohol, they cannot be conveniently weighed as such, but must be converted into sulphates. The amyl solution of the strontium may be precipitated at once with sulphuric acid, after adding sufficient alcohol to get a convenient mixture. As the barium bromide is not quite insoluble, the weight of the barium sulphate will be a trifle too low, whilst that of the strontium will be a little too high; the necessary correction, therefore, has to be made.

L. DE K.

Detection and Estimation of Minute Quantities of Lead in the presence of Copper and Iron. By F. L. TEED (*Analyst*, 17, 142—143).—The most delicate reaction for both lead and copper is, no doubt, ammonium sulphide, and the amount present can, of course, be estimated colorimetrically by comparison with known quantities. The objection to the use of ammonium sulphide is, however, that it does not distinguish between the two metals. To effect this distinction, the author makes use of the well-known fact that copper is not affected by ammonium sulphide in presence of potassium cyanide. To test for lead in lemonade, for instance, a measured quantity of the liquid is placed in a cylinder or white basin, and after adding a few c.c. of ammonia, mixed with a few drops of solution of potassium cyanide. If now a drop of ammonium sulphide is added the lead is precipitated, but not the copper or iron.

Lead may also be detected, but not estimated, in tartaric acid by burning this substance and digesting the ash with strong sulphuric acid, which will, of course, convert any lead into sulphate and dissolve it; the author discovered, some years ago, a most delicate test for lead in sulphuric acid, consisting in adding a drop of hydrochloric acid, or a crystal of common salt. Any lead is precipitated as chloride, giving a peculiar pearly opalescence. L. DE K.

Volumetric Estimations and Separations by means of Potassium Ferrocyanide and Ferricyanide. By C. LUCKOW (*Chem. Zeit.*, 16, 1428—1429; 1449—1450).—The author (compare Abstr., 1892, 1129, 1527) gives numerous instances where his process is useful for the quantitative estimation of a mixture of metals. As an example may be quoted the estimation of the constituents of an alloy of copper (5 per cent.), antimony (10 per cent.), and tin (85 per cent.). 1.2 grams of the alloy was dissolved in 12 c.c. of a mixture of 3 vols. of hydrochloric acid (sp. gr. 1.12) and 1 vol. of nitric acid (sp. gr. 1.2), with the aid of a gentle heat. Potassium chlorate was now added until the liquid had, even after 10 minutes, a decided odour of chlorine, showing that all the antimony had passed into the highest state of oxidation. After cooling and adding a little solution of tartaric acid, the mixture was put into a 100 c.c. flask, the beaker rinsed with some more tartaric acid, and the whole made up to the mark. 25 c.c. of this solution (= 0.3 gram alloy) was mixed with 10 c.c. of dilute sulphuric acid (1—10), and the copper was roughly titrated with a solution of potassium ferricyanide, 1 c.c. of which represented 0.00474 gram of Cu. The experiment was now, of course, repeated, and it was found that, after making an allowance of 0.4 c.c., 3.3 c.c. of ferricyanide was required, which gave 5.2 per cent. of copper instead of 5 per cent. 10 c.c. of the solution (= 0.12 gram alloy) was mixed with 10 c.c. of dilute sulphuric acid, and then with 8 c.c. of a solution of potassium ferrocyanide, 1 c.c. of which represented 0.0118 gram of Sn. After slightly warming for three minutes, the liquid had completely gelatinised. On adding 0.2 c.c. more ferrocyanide at the time, it was found that the iron test made its appearance when 9 c.c. had been used. The experiment was now most carefully repeated, 8.5 c.c. ferro-

cyanide being straightway added, and then further additions of 0.2 c.c. were made. It was found that the reaction was complete when 8.8 c.c. was used, and after allowing 0.1 c.c. this made 8.7 c.c., which calculated to metal gave 85.5 instead 85 per cent. of tin. If the antimony was simply taken from the difference, the analysis only took an hour, but a direct estimation was also performed as follows:—50 c.c. of the solution was mixed with a decided excess of potassium ferrocyanide. After filtering and washing the precipitate with weak brine, the antimony was precipitated with hydrogen sulphide, the precipitate dissolved in sodium sulphide and then electrolysed. 9.4 per cent. of antimony was obtained.

With a little ingenuity, the process described by the author may be so altered as to suit the assay of almost any kind of alloy. For the benefit of those who might like to try the method, the author has constructed a very useful table, showing the properties of the various metallic ferrocyanides and ferricyanides.

L. DE K.

Detection of Mercury in the Organism. By E. LUDWIG (*Chem. Centr.*, 1892, ii, 941; from *Pharm. Post*, 25, 1099—1101).—The organs are finely divided, weighed, and boiled for some hours with an equal weight of 20 per cent. hydrochloric acid, then cooled to 60°, and potassium chlorate added in portions of half a gram, whereby the dark liquid becomes clear; it is then cooled, thrown on a filter, the residue washed with water, and 5 grams of zinc dust added to the filtrate, which is then vigorously stirred for five minutes. It is kept for some hours with repeated agitation and a second portion of zinc dust is then added with vigorous stirring. The zinc is allowed to settle, the clear liquid poured off, the residue washed, first with water, then with the addition of a few drops of aqueous soda, and finally again with water. The residue is collected on a glass wool filter, treated with alcohol to remove water, and dried by suction in a stream of air. The mercury is then separated from the zinc dust by distillation and recognised as usual.

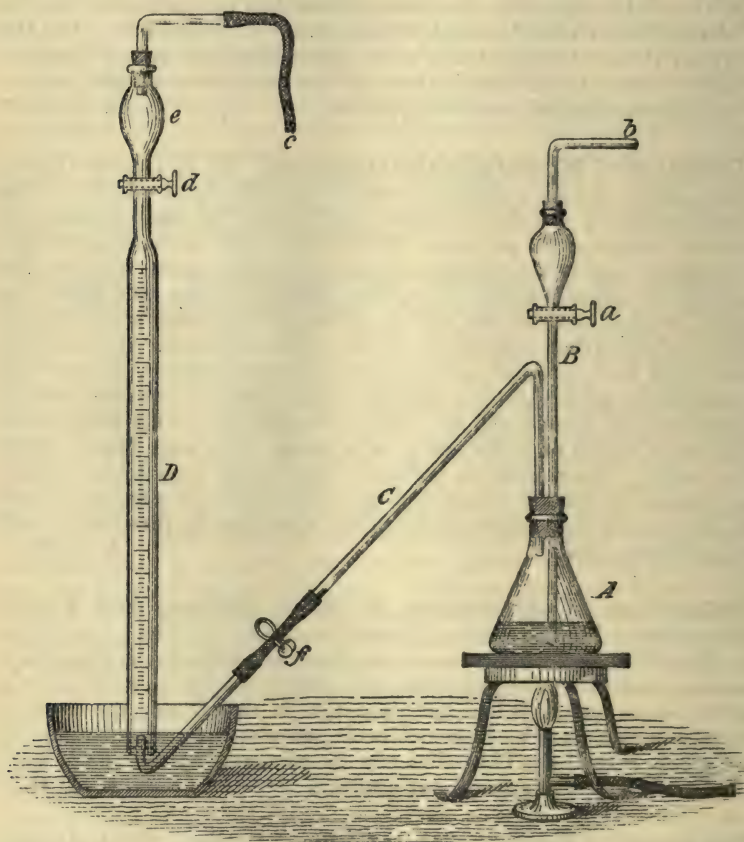
A. J. G.

Estimation of Aluminium in Steel, Bronze, and Ferro-aluminium. By P. ROZYCKI (*Chem. Centr.*, 1892, ii, 1047; from *Mon. Sci.*, 6, ii, 815).—0.2 to 2 grams of the finely divided alloy is placed in a platinum boat in a porcelain tube, and slowly heated to redness in a current of oxygen. When the oxidation is completed, the mass is ignited in a current of hydrogen chloride, when only the alumina, mixed with silica, remains. The silica can be removed by treatment with hydrofluoric acid and subsequent ignition.

A. J. G.

Behaviour of Ferric Oxide in Soil and Rocks. By R. SACHSSE and A. BECKER (*Landw. Versuchs-Stat.*, 41, 453—466).—Ferric oxide (not as silicate) in soils can be estimated by reducing with hydrogen, and measuring the hydrogen which is evolved by the action of the reduced iron on an acid. The substance containing iron is weighed in a platinum boat, the boat put into a wide glass tube and heated in a stream of hydrogen. While this is going on, water is boiled in the

flask *A* (see fig.) to drive out the air; when the reduction of the ferric oxide is complete, the boat is slipped out of the tube into the flask without interrupting the hydrogen evolution. The flask is closed with a cork provided with a funnel tube, *B*, and a delivery tube, *C*; the tap *a* is opened, and the tube *b* connected with a carbonic anhydride apparatus from which carbonic anhydride is passed into *A* until all the air is displaced. The end of the tube *C* is now placed under the measuring tube *D*, and the clamp *f* and the tap *a* closed. The funnel is filled with dilute, boiled sulphuric acid, the cork of *b* replaced and connected with the carbonic anhydride apparatus. The burner under



A is lighted and acid let in. By continued boiling all the hydrogen is driven into *D*. The measuring tube is then placed in a tall cylinder of water, the volume of gas read and reduced to 0° and 760 mm.

If the substance analysed contains silicates, these may be partly

decomposed with formation of ferric sulphate. This will redissolve a part of the metallic iron and yield ferrous oxide. In this case the contents of the flask are cooled in an atmosphere of carbonic anhydride, made up to 500 c.c., of which 250 c.c. is quickly filtered and titrated with permanganate. Some silicates, such as the micas, give ferrous oxide with hot dilute sulphuric acid. A correction for this is made by making one or more determinations without previously reducing with hydrogen.

Good results were obtained with pure ferric oxide; the introduction of ferric oxide with the sulphuric acid had no injurious effect. Good results were also obtained with ferric oxide mixed with biotite. With laterite and with two red soils no results could be obtained which were at all concordant; this was not due, as was shown by direct experiments, to the presence of hydrated silica, nor was sufficient organic matter present to account for the great differences. By prolonged heating of the red soil practically the whole of the ferric oxide disappeared. This can only be explained by the assumption that the ferric oxide was found in the soil as hydrated silicates or iron-kaolin; this would be reduced by hydrogen, but by ignition would be rendered difficultly decomposable.

Both ferric and ferrous oxides (especially ferrous) when ignited with hydrated silicates partly decompose, becoming at the same time converted into silicates. This was shown to be the case by heating mixtures of ferric oxide with kaolin, apophyllite, and analcime respectively; with eläolite the reaction did not take place, and the whole of the iron was removed.

N. H. M.

Detection of Gold in Dilute Solution. By T. K. ROSE (*Chem. News*, 66, 271).—The purple of Cassius reaction may be successfully applied in a test-tube to detect gold in solutions containing as little of this metal as 1 in 4,000,000, whilst with more dilute solutions, by employing a greater bulk of liquid (3 litres or so) and pouring it, when heated to boiling, into a large beaker containing 10 c.c. of a saturated aqueous solution of stannous chloride, acidified with hydrochloric acid, so as to mix the two liquids as rapidly as possible, a distinctly purple precipitate has been obtained with a 1 per 100,000,000 solution. The reaction is not disturbed by the presence of sodium chloride, calcium sulphate, potassium chloride, potassium bromide, or ammonium chloride, either separately or all together; it may be applied, therefore, for testing sea water for gold precipitable by stannous chloride.

D. A. L.

Volumetric Estimation of Sulphates in Potable Waters.—By D. VITALI (*L'Orosi*, 1892, 260—262).—The volumetric process devised by the author for estimating the metals of the alkaline earths (Abstr., 1892, 1521) is applicable in a reversed form to the determination of dissolved sulphates. A known volume of N/10 barium chloride solution is added to the liquid to be titrated, the barium sulphate filtered off, and one-half of the volume of the liquid before filtration collected. The excess of barium in this is then found by titration with N/10 sodium carbonate solution as described in the paper above

mentioned. The solution must be neutral and, of course, free from substances which precipitate barium.

For the estimation of sulphates in potable waters, 500 c.c. of the boiling water is made alkaline with sodium carbonate solution; after filtration, the filtrate and washings are evaporated to 50 c.c., and the boiling solution accurately neutralised with acetic acid. 25 c.c. of N/10 barium chloride solution is now added and the solution filtered; one-half the previous volume of the solution is collected and the excess of barium estimated by titration with sodium carbonate solution. No allowance is made for the volume of the barium sulphate precipitate.

W. J. P.

Cyanogen Iodide and Sodium Thiosulphate. By C. MEINEKE (*Zeit. anorg. Chem.*, 2, 157—164).—E. v. Meyer (Abstr., 1888, 242) stated that cyanogen iodide is decomposed by hydrogen iodide and by sulphurous acid, and proposed to make use of these reactions for the volumetric estimation of cyanogen iodide. He did not, however, adduce experimental proof, but this is now brought forward by the author as regards the more complicated reaction between cyanogen iodide and sodium thiosulphate. A known weight of cyanogen iodide, dried over sulphuric acid and subsequently sublimed at the lowest possible temperature, was dissolved in a known weight of water, and potassium iodide (1 gram) and hydrochloric acid (sp. gr. 1.12; 1 c.c.) added to weighed quantities of the solution, containing 0.3—0.4 gram of cyanogen iodide; the liberated iodine was then estimated by ascertaining the weight of a standard solution of sodium thiosulphate required to reduce it. The results obtained were in accordance with the equation $2\text{CNI} + 4\text{Na}_2\text{S}_2\text{O}_3 + 2\text{HCl} = 2\text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaCl} + 2\text{NaI} + 2\text{HCN}$. In neutral solutions, however, cyanogen iodide (3 mols.) reacts with sodium thiosulphate (5 mols.), giving rise to sodium sulphate (1 mol.). The author believes that the last-named salt is produced by a secondary reaction between the alkali cyanide and tetrathionate.

Potassium cyanide may be titrated with standard acid and methyl-orange, the liberated hydrogen cyanide being without action on the indicator.

A. R. L.

Estimation of Cyanogen in Iodine. By C. MEINEKE (*Zeit. anorg. Chem.*, 2, 168—174).—The author finds that cyanogen may be estimated in iodine (1) by ascertaining the difference in titrating with thiosulphate in acid and neutral solutions, (2) by gravimetrically determining the amount of sulphate produced on reducing the cyanogen iodide in neutral solution (compare preceding abstract). The results are not very accurate.

A. R. L.

Detection of Cyanogen in Iodine. By C. MEINEKE (*Zeit. anorg. Chem.*, 2, 165—167).—Varying amounts of cyanogen iodide were added to saturated aqueous solutions of iodine, so that the total volume was 20 c.c. The mixture was acidified with a drop of dilute hydrochloric acid, and reduced with such a quantity of sodium thiosulphate that a slight yellow coloration was left. On now adding

ferrous sulphate and alkali, a precipitate of Prussian blue is formed. The limit of the test was found to be 1 part of cyanogen in 54,000 parts of water.

When a neutral solution of iodine containing cyanogen iodide and a small quantity of potassium iodide is treated with centinormal thio-sulphate until the yellow colour has almost disappeared, and a 0.1 per cent. solution of starch added, the well-known iodide of starch reaction becomes apparent after a while. A more reddish tone is, however, obtained than that produced by solutions of pure iodine. The presence of 0.008 gram of cyanogen iodide in 20 c.c. of water may be detected by the formation of a precipitate of barium sulphate on adding barium chloride to the last-mentioned solution after the addition of thiosulphate (compare preceding abstracts).

A. R. L.

Oxidation of Glycerol in Acid Solution. By S. SALVATORI (*Staz. Sper. Agrar.*, 21, 130—140).—Experiments, suggested by Olivieri and Spica's method for the estimation of glycerol in wine (*Abstr.*, 1891, 369), were made on the oxidation of glycerol by permanganate: a solution containing 0.1062 per cent. of glycerol was employed. To 10 c.c. of this solution, acidified with sulphuric acid, the permanganate was added as long as the colour disappeared, the addition being stopped when the colour produced by 2 or 3 drops was no longer destroyed by continued heating of the solution on a water-bath. The results obtained were rather high. Although the action was much more rapid, similar results were obtained when the solution was actually boiled, instead of heating it on a water-bath, and also when increased amounts of acid were employed. The employment of permanganate in excess gave rise to increased reduction. Finally, when stronger solutions of glycerol were used, the amount of permanganate reduced was found to increase at a still greater rate; thus, whilst 10 c.c. of 0.01 per cent. glycerol reduced 10.5 c.c. of permanganate solution, the same amount of 0.05 per cent. glycerol reduced 67 c.c.

After discussing the various methods employed for the oxidation of glycerol (compare Legler, *Chem. Zeit.*, 1886; Cross and Bevan, *Chem. News*, 1887, 2; and Planchon, *Compt. rend.*, 107, 246), the author describes the following methods in which he adopted Planchon's reaction (*loc. cit.*):—

The apparatus consists of a small, wide-mouthed flask, furnished with a reflux condenser, the upper end of which is connected with the upper end of a burette; the lower end of the burette is connected by means of india-rubber tubing with a second tube; both these tubes are connected with a large bulb. The burette is surrounded by a second tube, and kept cool by means of cold water. The analysis is carried out as follows:—The necessary amounts of permanganate (20 c.c. of 5 per cent. solution) and sulphuric acid (10 c.c. of 30 per cent. acid) are put into the flask, then a tube containing the glycerol solution (10 c.c.) is carefully put in, so as not to overturn it. The flask is connected with the condenser and immersed in cold water. The measuring apparatus is then filled with mercury and connected with the condenser. The same water is made to pass through the

vessel containing the flask, through the condenser, and through the burette water jacket, so that the temperature is everywhere the same. The flask is taken out of the water-bath, dried, the tube containing the glycerol overturned, and the whole of the contents mixed; the reaction is finished in a minute or two. The whole apparatus is again cooled, and the increase of volume due to the carbonic anhydride formed is read off and reduced to 0° and 760 mm. pressure. A smaller amount of glycerol solution may be employed, but it is best always to keep to the amounts of permanganate and acid already given. The strength of glycerol solution may vary from 0.05 to 2 per cent. In analysing wine or beer, the amount of glycerol should be approximately ascertained before employing this method.

N. H. M.

Estimation of Glycerol in Wine and other Fermented Liquids. By S. SALVATORI (*Staz. Sper. Agrar.*, 21, 141—145).—50 c.c. of red wine is treated with basic lead acetate, the excess of lead precipitated by sodium carbonate, and the filtered liquid evaporated to about 10 c.c. It is then treated with a mixture of quicklime and anhydrous gypsum, powdered, and extracted with alcohol. The alcoholic solution is evaporated to 10 c.c., mixed with ether (15 c.c.), filtered if necessary, and evaporated to a small bulk. Water is then added to the residue, and the mixture boiled to drive off the alcohol, evaporated to about 10 c.c., and distilled in the apparatus used by v. Törring (*Abstr.*, 1889, 735). A little water is subsequently distilled, in order to remove the last traces of glycerol from the neck of the retort. The glycerol in the distillate, made up to 50 c.c., is determined as already described (see preceding abstract).

The same process is employed with dry white wines. With sweet wines and beer, 100 c.c. is used for the analysis; the distillate is made up to 50 c.c.

The chief difficulty in the process is to get the whole of the glycerol in a state of purity; the alcohol is liable to extract compounds of glucoses with lime, which are not precipitated by ether; on the other hand, if the evaporation and precipitation with ether is repeated, there will be a loss of glycerol.

N. H. M.

Metaphosphoric acid as a Precipitant of Proteïds in the Estimation of Sugar in Milk. By G. DENIGÈS (*Bull. Soc. Chim.* [3], 7, 493—499).—For the optical determination of sugar in milk, 10 c.c. of the sample is mixed with a 5 per cent. solution of sodium metaphosphate (1.5 c.c.), hydrochloric acid (0.3 c.c.), and some water added, and, after well agitating the mixture, it is diluted to 50 c.c., filtered, and the filtrate examined by the polarimeter in a 500 mm. tube. Metaphosphoric acid is stated to exert no influence on the rotatory power of milk sugar.

A. R. L.

New Method for the Estimation of Grape Sugar. By A. W. GERRARD (*Pharm. J. Trans.* [3], 52, 208—210).—When to a volume of Fehling's solution there is added just sufficient potassium cyanide to discharge the blue colour, and the liquid is mixed with a second

equal volume of Fehling's solution, grape sugar will produce no precipitate in the boiling mixture, but its gradual addition causes a steady disappearance of the blue colour, and at the sharp end change the glucose value will be found approximately equal to half that of ordinary Fehling's solution. The author's explanation is, that the double potassium and copper cyanide formed in the first instance, being a solvent of the cuprous oxide, prevents its precipitation when formed by the action of the glucose on the second volume of the Fehling, in which reduction is presumed to take place as in the ordinary method. In practice, he keeps three solutions in separate bottles, as follows:—(1) Copper sulphate, 69·3 grams, water to 500 c.c. (2) Rochelle salt, cryst., 175 grams; sodium hydroxide, 76·56 grams, water to 500 c.c. (3) Potassium cyanide, 33 grams (or a sufficiency), water to 500 c.c. For testing, 5 c.c. of each solution is mixed with 50 c.c. of water, and to this liquid, boiling in an open vessel, the grape sugar is added until the blue colour disappears. It returns shortly afterwards by absorption of oxygen from the air, but this does not affect the accurate observation of the end reaction. In case any precipitate is formed, the cyanide solution must be strengthened. The author had kept some of this solution for three months without change. In the discussion following the paper, it was suggested that glycerol might advantageously replace the alkaline tartrate.

R. R.

Estimation of Starch. By GUICHARD (*Bull. Soc. Chim.* [3], 7, 554—560).—The following method is recommended by the author for the estimation of starch in cereals. The flour (5 grams ?) is boiled in a reflux apparatus with a saturated solution of oxalic acid (90 c.c.) for a quarter of an hour; the solution now contains soluble starch, dextrin, and a little glucose. Nitric acid (10 c.c.) is then added, and a portion of the filtrate boiled for an hour in a reflux apparatus and polarised. The amount of glucose thus obtained is converted into starch by multiplying by 0·9. The insoluble residue, after washing, is free from starch. The results need none of the corrections that are necessary in other saccharification methods, since only traces of nitrogenous matters are dissolved, and much less cellulose is attacked than by the use of nitric acid alone. When cellulose, in the state of raw material, is boiled with nitric acid for an hour, the liquid reduces Fehling's solution, and is optically active; after repeating the operation several times, however, with fresh quantities of acid, a liquid is finally obtained which exerts no effect on Fehling's solution. The substances saccharified are lignin, incrusting matters, pectin-like substances, gummy matters, and sugars. Vegetable ivory is more readily attacked than any other cellulose in the form of raw material. The residue left undissolved from these operations is not pure cellulose, but contains hydrocellulose, besides a small quantity of nitro-compounds which can be partially removed by washing with alcohol and ether. Hydrocellulose is distinguished from oxycellulose by its incapability of fixing colouring matters, but the two compounds behave similarly towards Fehling's solution. Sulphate of iron gives a rusty precipitate on boiling with hydrocellulose.

A. R. L.

Detection of Wheat-flour in Rye-flour. By A. KLEEBERG (*Chem. Zeit.*, 16, 1072—1073).—The author recommends the following simple method, based on the peculiar behaviour of wheat gluten. A pinch of the suspected flour is put on an object glass, 7.5 cm. long and 2.5 cm. wide, and well mixed with 5 or 6 drops of luke-warm water. It is very important there should be enough water to float the starchy particles, as the experiment will fail if a paste has formed. The mixture is now spread over $\frac{2}{3}$ — $\frac{3}{4}$ of the object glass, and a second slide is put over it in such a way that the free end of the one lies at the right, and of the other at the left, side. The slides are now firmly pressed together, wiped dry, and then passed several times over each other. Already, when pressing the plates, whitish superficies make their appearance, and on moving the plates they readily roll out. If much wheat-flour is present, the rods are long and thick, but if there is only a little of it, they are short and thin. With a little practice, the operator will be able to easily detect an admixture of 5 per cent. of wheat-flour.

L. DE K.

Estimation of Acetone in Urine. By R. SUPINO (*L'Orosi*, 1892, 217—221).—The action of iodine and caustic alkali on acetone, represented by the equation $\text{CO}(\text{CH}_3)_2 + 3\text{I}_2 + 4\text{NaHO} = \text{CHI}_3 + \text{CH}_3\text{COONa} + 3\text{NaI} + 3\text{H}_2\text{O}$, forms the basis of the following method of estimating acetone when present in urine. On distilling the urine, the acetone comes over with the first runnings; potash or soda and a solution of iodine in potassium iodide are then added to this fraction until the brown colour is persistent; the colour is then discharged by soda, and the solution extracted with ether until the aqueous layer loses its turbidity. The ethereal solution is separated, evaporated to dryness, the residual iodoform dissolved in concentrated alcohol and boiled for 20 minutes with caustic soda free from chloride in a reflux apparatus, when the reaction represented by the equation $\text{CHI}_3 + 4\text{NaHO} = 3\text{NaI} + \text{H}\cdot\text{COONa}$ occurs. The alcohol is now evaporated, the aqueous solution acidified with dilute nitric acid, and excess of N/10 silver nitrate solution added; the silver iodide is filtered off, and the excess of silver nitrate determined by titration with standard potassium ferrocyanide solution, using ferric sulphate as an indicator. The method gives good results.

W. J. P.

Estimation of Lactic acid in Milk. By W. THÖRNER (*Chem. Zeit.*, 16, 1469—1470; 1519—1520).—The author again calls attention to a process which he has used since 1887, and which has also been independently worked out by Pfeiffer. 10 c.c. of the sample is diluted to 30 c.c. with distilled water, and mixed with 5 drops of a 5 per cent. alcoholic solution of phenolphthalein. Decinormal soda is now added from a delicate burette until the liquid is decidedly reddish. If a milk should take 1 c.c. of the alkali, the author calls this 10° of acidity. If no distilled water is at hand, common water may be used after five minutes boiling to drive off any carbonic anhydride.

Fresh milk usually shows 8—16° of acidity. When the acidity reaches 22°, the milk coagulates on boiling.

L. DE K.

Estimation of Oleïc acid. By O. HEHNER (*Analyst*, 17, 181—183).—The author investigated the well-known process based on the separation of lead oleate from the lead salts of fixed fatty acids by means of ether. The oleïc acid obtained by decomposing the ethereal solution by means of hydrochloric acid was in no case pure, as its iodine absorption varied from 58 to 100 per cent., 90 per cent. being its theoretical number. On the other hand, the acids liberated from the insoluble lead salts absorbed a considerable amount of iodine, ranging from 18 to 35 per cent., showing the presence of a considerable amount of oleïc acid. The figures show most conclusively to the author's mind that the method of oleïn determination founded on the relative solubilities of the lead salts in ether is utterly untrustworthy.

L. DE K.

Estimation of Oleïc acid. By L. DE KONINGH (*Chem. News*, 65, 259).—Oleïc acid may be estimated with great accuracy in fats of the ordinary type, by means of the ether method (compare preceding abstract); but, in order to get trustworthy results, it is necessary to decompose the insoluble lead salts by means of hydrochloric acid, and to recrystallise the fatty acids so obtained from hot alcohol. The mother liquor will generally contain a small quantity of oleïc acid, which may be recovered by converting it into a lead salt and extracting this with ether. The author further states that the lead salts of stearic and palmitic acids are absolutely insoluble in cold ether, and sees no sufficient cause to abandon the lead-ether method.

L. DE K.

Estimation of Cholic acid in Bile. By LASSAR-COHN (*Ber.*, 26, 146—151).—See this vol., ii, 220.

Estimation of Fat in Milk by Babcock's Method. By A. W. STOKES (*Analyst*, 17, 127—130).—This process is almost identical with Leffmann and Beam's method (*Abstr.*, 1892, 1532). Milk is mixed with an equal bulk of strong sulphuric acid in a bottle with a graduated neck, and, whilst hot, whirled for eight minutes in a centrifugal apparatus making 500 revolutions per minute. After filling with hot water to the beginning of the neck, they are again whirled for two minutes. More hot water is now added up to the top of the neck; another two minutes whirling is given, and the fat which by this time has collected in the neck is read off without delay.

The results obtained by the author can hardly be called satisfactory, although the process may be recommended as a rough-and-ready method.

L. DE K.

Babcock's Method of Milk Analysis. By F. T. SHUTT (*Analyst*, 17, 227—229).—The author, who has extensively used this process (see preceding abstract), states that when the Babcock test is made according to the instructions given with the machine, strictly trustworthy results are obtained. His test analyses are certainly satisfactory (also compare *Abstr.*, 1891, 1339).

L. DE K.

Estimation of Total Solids in Milk. By H. D. RICHMOND (*Analyst*, 17, 225—227).—Although the numerous processes now in use are sufficiently accurate for technical purposes, scientifically accurate results cannot be obtained. The author thinks, however, that the following process is a step in the right direction:—3 grams of asbestos, best quality, is ignited in a platinum dish in a muffle, and the whole is weighed. 5 grams of milk is added, and the dish is placed for two hours on the water-bath. After drying for 12 hours in a water-oven at 98°, the author has always succeeded in getting a perfectly constant weight.

The residue serves excellently for the purpose of ash estimation.

L. DE K.

Estimation of Butter Fat in Milk. By L. G. PATTERSON (*Exper. Stat. Record.*, 4, 267; from *Mississ. Stat. Bul.*, No. 21, 1892).—The method is a modification of Beimling's. The Beimling centrifugal and test bottles are used, and the milk (15 c.c.) is treated with 1.5 c.c. of amyl alcohol (instead of amyl alcohol and hydrochloric acid). The bottles are whirled for a minute, nearly filled with hot water, again whirled for half a minute, and the columns of fat read off. The results obtained by the method were sometimes higher and sometimes lower than those obtained by the original method, the differences averaging 0.03 per cent. The advantages of the new method are: (1) a sharply defined fat column, (2) the absence of charring of the fat, (3) the contents of the bottles never foam over, (4) quickness, (5) cheapness.

N. H. M.

Volumetric Estimation of Alkaloids. By A. H. ALLEN (*Chem. News*, 66, 259).—The author points out that the neutrality of phenolphthaleïn towards, and its application in the estimation of, many alkaloids (compare Barthe, this vol., ii, 146) was mentioned by him and commonly known in 1891. When applied in the method of analysis of a mixture of cinchona alkaloids, in which the cinchonidine is precipitated by a neutral solution of sodium potassium tartrate, the precipitate is washed once with a saturated solution of the precipitant, instead of with water as is usually done, is then immersed in boiling water and titrated with N/20 alkali, using phenolphthaleïn as indicator, and inasmuch as the latter is neutral to Rochelle salt, whilst the cinchonidine tartrate acts towards it like free tartaric acid, the alkaloid may in this way be readily estimated. Quinidine hydriodide can be estimated in a similar manner. Methyl-orange, owing to its neutrality towards alkaloids and organic bases, may be used as an indicator for the titration of these substances, urea, caffeine, theobromine, and perhaps aniline excepted. The ethereal solution of the alkaloid is placed in a stoppered cylinder with aqueous methyl-orange, and titrated with N/50 hydrochloric acid.

D. A. L.

General and Physical Chemistry.

Separation and Striation of Rarefied Gases under the Influence of the Electric Discharge. By E. C. C. BALY (*Phil. Mag.* [5], 35, 200—204).—On passing an electric discharge through a vacuum tube containing a small quantity of hydrogen, the hydrogen lines are only observed in the spectrum of the negative glow, and not at all in the body of the tube. This the author shows to be due to accumulation of the hydrogen round the negative pole; by employing conveniently shaped tubes containing mixtures of carbonic anhydride and hydrogen at about $\frac{3}{4}$ mm. pressure, so complete a separation of the hydrogen ensues that, on sealing off the portion of the tube containing the positive pole, it is found to show only a trace of hydrogen by spectroscopic tests. Mixtures of hydrogen with other gases, such as nitrogen, carbonic oxide, sulphurous anhydride, iodine, or mercury vapour, behave in a precisely similar manner to the above. In a tube containing carbonic oxide and carbonic anhydride, the former gas separates at the negative pole, whilst with a mixture of carbonic anhydride and nitrogen, very complete separation of the carbonic anhydride occurs; sulphurous anhydride is separated from a mixture of that gas with carbonic anhydride. Air has to be highly rarefied before separation occurs, and then the oxygen seems to go to the negative pole; no relation could be established between the separation of the various gaseous mixtures and the molecular weights of their constituents.

There seems to be some connection between this kind of separation and striated discharges; strongly marked striæ are only observed when separation occurs, and not if the contents of the tube remain homogeneous. If the formation of a glow round the negative pole be prevented by making the latter a mere point, no striation or separation is observed. Pure gases do not stratify, iodine, sulphur, arsenic, and mercuric iodide giving only a phosphorescence throughout the tube. Hydrogen, prepared in a state of considerable purity, showed but traces of striation. The author concludes that pure hydrogen would not stratify at all, and that striation generally is due to the separation of two gases.

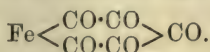
W. J. P.

Atomic Refractions of the Elements with respect to Sodium Light. By F. ZECCHINI (*Gazzetta*, 22, ii, 592—604).—The increasing application of Pulfrich's total refractometer to the determination of refraction constants renders a knowledge of the atomic refractions of the elements with respect to the D ray of great importance. The author has therefore calculated these constants from a large number of measurements made on organic compounds by several observers, and has tabulated the results in the present paper. The following table contains the values thus arrived at:—

	$\frac{n_D - 1}{d}$		$\frac{n_D - 1}{d}$
Carbon	4.71	Bromine	15.34
Hydrogen	1.47	Iodine	25.01
Alcoholic oxygen..	2.65	Increase for each	
Aldehydic „ ..	3.33	double bond.....	2.64
Chlorine.....	10.05		

W. J. P.

Molecular Refraction and Dispersion. By J. H. GLADSTONE (*Phil. Mag.* [5], 35, 204—210).—The author has measured the refraction constants of ferropentacarbonyl (compare Abstr., 1891, 1322), and considers that his results favour Mond's suggestion that this substance is a ring compound having the constitution



The molecular refraction for the α hydrogen line is about 68.5, and the molecular dispersion between the γ and α hydrogen lines is 6.6; the molecular dispersion of each carbonyl group is 1.3, the value shown by this group in nickel tetracarbonyl (compare Armstrong, *Proc.*, 1893, 57).

The author has calculated the atomic refractions of indium and gallium from the later observations of Soret on the alums of these metals (*Arch. Sci. Phys. Nat., Genève*, 14, 96). For indium, $R_A = 13.7$, and for gallium, $R_A = 11.6$.

Calculations of the atomic refraction of sulphur from observations made on the element in the three states, and on its simple compounds with carbon and the halogens, give very similar results; the values are lower than those deduced from measurements made on certain organic sulphur compounds by Nasini and Costa (Abstr., 1891, 1305; 1892, 34).

The refraction equivalents of liquid oxygen and ethylene, as determined by Liveing and Dewar (this vol., ii, 201), agree well with the theoretical numbers; the refractive indices of liquid nitrous oxide seem to indicate that the nitrogen in this substance is in the same condition as in the nitriles (compare Armstrong, *loc. cit.*).

W. J. P.

Spectrochemistry of Nitrogen. By J. W. BRÜHL (*Ber.*, 26, 806—809).—By subtracting from the molecular refraction of a nitrogenous compound the sum of the atomic refractions of the atoms other than nitrogen contained in it, these atomic refractions being assumed to be the same as those they have in the free state, the atomic refraction of the nitrogen atom itself is calculated. This for yellow light is found to be: singly bound (in ammonia), 2.50; doubly (in nitrous oxide), 2.27 at least; triply, or fivefold? (in free nitrogen), 2.21. The values do not continuously increase, as in the case of carbon; hence it is argued that "single, double, and triple linking of carbon atoms is something quite different in its nature from single, double, and triple linking of nitrogen atoms." Compounds containing the group C:N have a molecular refraction greater than that cal-

culated, and the same is true for cyanogen, which contains the group $C\equiv N$. But, strangely enough, hydrogen cyanide has a molecular refraction about equal to the calculated value; hence this gas cannot contain the group $C\equiv N$, and "cyanogen and hydrogen cyanide cannot have a similar constitution."

C. F. B.

Influence of Temperature on the Rotatory Power of Liquids.

By A. COLSON (*Compt. rend.*, **116**, 319—322).—A continuation of the discussion with Friedel. When aniline is dissolved in diacetyl-tartaric acid or its anhydride, the solution is lævogyrate, whereas it might have been expected that it would be dextrogyrate, since C_6H_5N is heavier than $C_2H_3O_2$. It is, of course, possible that molecular combinations are formed with the excess of aniline, but any objection on this ground would be equally fatal to all the evidence obtained from solutions in alcohol or benzene.

The rotatory power of isobutylic isoamylic oxide changes sign at a very low temperature, and the results obtained with this and two similar liquids are given in the following table, and it will be observed that as the temperature rises, diisoamylic oxide shows a maximum of rotatory power, and methylic amylic oxide passes through a minimum:—

Temperature ..	-40° .	-21° .	-4° .	$+15^\circ$.	$+40^\circ$.	$+100^\circ$.
Isobutylicisoamylic oxide	$-0^\circ 6'$	$+0^\circ 4'$	$+0^\circ 11'$	$+0^\circ 13'$	$+0^\circ 15'$	—
Diisoamylic oxide	?	$+0 21$	$+0 35$	$+0 42$	$+1 3$	$+1^\circ 16'$
Methylic isoamylic oxide	$+1^\circ 4'$	$+0 10$	$+0 12$	$+0 20$	$+0 28$	—

It would seem that chemical constitution is not necessarily the preponderating factor in determining either the sign or the value of the rotatory power, but physical causes may produce considerable variations in the optical activity of certain liquids.

C. H. B.

Stereochemistry. By C. FRIEDEL (*Compt. rend.*, **116**, 351—353).—

A continuation of the discussion with Colson.

C. H. B.

Alteration of the Sign of Optical Rotation. By J. A. LE BEL (*Bull. Soc. Chim.* [3], **7**, 613—649).—A polemical paper.

Electrochemical Investigations. By F. EXNER (*Monatsh.*, **13**, 851—871).—The author has determined the potential differences between metals and bases, making use of the method employed for the like determination in the case of the acids. The metals all become negatively charged, and the solutions positively. The potential differences are of the same order of magnitude as those observed for solutions of acids and salts. The values increase with potash and soda very considerably, with rise in concentration with all metals, except magnesium, the values for which are nearly all lower than those obtained in pure water. The occurrence of a maximum at a certain concentration, so frequently noticed in the case of the acids, was not observed with the bases, except in the two cases of mercury

and tin in ammonia solutions. With the acids, the potential differences were found to vary periodically with the atomic weights of the metals, so that certain metals always gave maximum and minimum values; a like behaviour is to be observed in the case of the bases.

With the aid of the numbers obtained for the potential differences between metals and acids and metals and bases, the author has been further able to determine potential differences between acids and bases. It is found that bases in contact with acids become negatively charged, and that acids therefore behave towards bases as they do towards the metals. Only one exception was noticed, in the case of acetic acid and ammonia, where the acid in very concentrated solution becomes feebly negative. Concentration exercises a very marked influence in all cases, a constant increase in the potential differences with increase of concentration being observed for hydrochloric, hydrofluoric, and acetic acids. Increase to a maximum with subsequent decrease was noticed for sulphuric, nitric, hydrobromic, and oxalic acids.

H. C.

Electrometric Study of Potassium Hydrogen Triplatohexanitrite. By M. VÈZES (*Compt. rend.*, 116, 185—188).—The author has measured the electrical conductivity of dilute solutions of potassium hydrogen triplatohexanitrite, $\text{Pt}_2\text{O}(\text{NO}_2)_6\text{K}_2\text{H}_4 + 3\text{H}_2\text{O}$, mixed with various proportions of potassium hydroxide (compare this vol., ii, 213). The normal salt corresponds with the mixture, $\text{Pt}_2\text{O}(\text{NO}_2)_6\text{K}_2\text{H}_4 + 4\text{KOH}$, but as the dilution increases it is stable only in presence of a greater and greater proportion of alkali. In the dilute solutions, several days are required before the liquid attains a condition of equilibrium, and the time required increases with the degree of dilution.

C. H. B.

Relation of Volta Electromotive Force to Pressure. By G. GORE (*Phil. Mag.*, [5], 35, 97—112).—A vertical glass tube, some 3 metres long, is filled with an electrolyte and closed by two similar electrodes, by means of which circuit with a galvanometer is completed; on allowing the tube to remain undisturbed until all sign of current, or variation of current, ceases and then reversing the two ends of the tube, sufficient potential difference is set up to cause considerable deflection of a Thomson's reflecting galvanometer. A large number of different metallic electrodes and of electrolytes, such as solutions of salts and acids, were employed, and in nearly every case an appreciable current was developed; the E.M.F. established is about 0.005 volt. The deflection of the galvanometer does not attain a maximum for some 5—10 minutes after reversing the position of the tube; this maximum deflection when once established diminishes very slowly, and, in a test case, had only decreased by one-third after 16 hours. A concentrated electrolyte is more active than a dilute one.

A number of experiments were made showing conclusively that the development of the current is due solely to the pressure of the column of electrolyte; the author finally discusses his results in their

relation to the work of Gibault on the change of E.M.F. accompanying increase of pressure in various cells (*Compt. rend.*, **113**, 465).

W. J. P.

Behaviour of Electrolytes in Mixed Solvents. By A. J. WAKEMAN (*Zeit. physikal. Chem.*, **11**, 49—74).—The author has found the following numbers for the relative speeds of the ions in aqueo-alcoholic solutions:—

Percentage of alcohol.	H.	K.	Na.	Cl.
50	101·8	23·9	20·1	24·7
40	128·1	27·6	21·9	28·4
30	156·4	32·4	24·6	33·6
20	197·3	39·3	29·1	40·7
10	242·7	49·7	36·7	51·3
0	320·5	67·9	45·5	73·5

The electrical conductivities of a number of organic acids in such solutions were determined, and from the results obtained it appears that Ostwald's formula $\frac{m^2}{(1-m)v} = k$, which is very accurate when the acids are dissolved in water, is not in this case valid. Acetone influences the dissociation of a substance in water in the same way as alcohol does, but in a greater degree.

Experiments were also made on the effect of alcohol in reducing the rate of inversion of sugar solutions by acids. There is no definite relation between the influence on the molecular conductivity and on the reaction velocity. It is possible that this difference is due to the change in the viscosity of the liquid occasioned by the addition of the alcohol.

Numerous tables and curves of the results are given by the author.

J. W.

The Temperature of Explosion. By A. MITSCHERLICH (*Ber.*, **26**, 399—403; compare this Journal, 1877, i, 42; this vol., ii, 202).—The temperature of explosion of a mixture of hydrogen and oxygen in the proportion of 2 : 1 by volume is found to vary with the pressure and with the shape of the containing vessel. For one and the same vessel, however, and for pressures less than 760 mm., the temperature of explosion falls as the pressure of the gaseous mixture is diminished, and the fall in temperature is proportional to the diminution of pressure. With pressures higher than 760 mm., great experimental difficulties are encountered, and the only certain conclusion that can be drawn from the experiments is that the temperature of explosion of gases is higher when they are compressed than when they are uncompressed. This is directly contrary to hitherto accepted views.

C. F. B.

Ignition Temperature of Explosive Gaseous Mixtures. By F. FREYER and V. MEYER (*Zeit. physikal. Chem.*, **11**, 28—37; compare Abstr., 1892, 680).—The authors have studied the temperatures at which various explosive gaseous mixtures ignite, using for low

temperatures an oil-bath, and for higher temperatures boiling sulphur (448°), phosphorus sulphide (518°), stannous chloride (606°), zinc bromide (650°), and zinc chloride (730°). The mixtures were either led through a tube immersed in the bath, or were enclosed in bulbs which were suddenly plunged into the hot liquid or vapour. The following results were obtained. The mixture did not explode at the lower temperature in each column, but did so at the higher.

Equivalent mixtures.	Free current.	Closed bulbs.
Hydrogen, oxygen.....	650—730°	530—606°
Methane, oxygen	650—730	606—650
Ethane, oxygen	606—650	530—606
Ethylene, oxygen	606—650	530—606
Carbon monoxide, oxygen ...	650—730	650—730
Hydrogen sulphide, oxygen..	315—320	250—270
Hydrogen, chlorine.....	430—440	240—270

It appears from these experiments that ignition always takes place at a lower temperature when the mixture is in a closed vessel than when passing freely through an open tube. If, however, an open vessel containing the gas is heated suddenly, the explosion takes place at the lower temperature. The speed of the current was so small that the difference cannot be explained by the gases being insufficiently heated.

J. W.

Temperatures of Explosion of Gaseous Mixtures. By V. MEYER (*Ber.*, 26, 428—429).—The temperature of explosion of a mixture of hydrogen and chlorine has already been shown by the author and Freyer (preceding abstract) to be very irregular. When bulbs, filled with this mixture, are dipped suddenly in the dark into boiling dimethylaniline (b. p. 193°), explosion generally occurs, but not always; whereas by employing boiling aniline (b. p. 182°) the mixture only exploded in two out of 40 experiments. Small quantities of admixed foreign gases, as well as the nature of the vessel enclosing the mixture, are of considerable influence.

A. R. L.

Specific Heat of Liquid Ammonia. By C. LUDEKING and J. E. STARR (*Amer. J. Sci.* [3], 45, 200—202).—The specific heat of liquid ammonia was directly determined, about 10 grams of the liquid being enclosed in a steel cylinder weighing nearly 71 grams, the whole heated to the boiling point of carbon bisulphide, and then dropped into a brass calorimeter whose water value was 1.36 cal.; it contained 150 grams of water at about 25°. Experiments were also made in which the cylinder and contents were first cooled in melting ice, and then introduced into the warm calorimeter water. Three determinations were made by each of the above methods, the average value for the specific heat of liquid ammonia obtained from the whole series being 0.8857.

H. C.

Specific Heats of Erythritol and Mannitol. By W. LOUGUININE (*Ann. Chim. Phys.* [6], 27, 138—144).—The author has made certain improvements in the apparatus previously described (*Ann. Chim.*

Phys. [5], 27, 398), and has now employed it in determining the specific heats of erythritol and mannitol respectively. The specific heat of erythritol was found to be 0.3520 as the average of three experiments, in which the maximum difference amounted to 0.54 per cent.; that of mannitol proved to be 0.3277 as the average of five experiments with a maximum difference of 1.13 per cent., or, neglecting one obviously incorrect result, 0.3287 as the average result of four experiments with a maximum difference of 0.3 per cent. The determinations were made between 100° and 20°. F. S. K.

Heat of Formation of Aragonite. By H. LE CHATELIER (*Compt. rend.*, 116, 390—392).—The heat of formation of aragonite and calcite was determined by dissolving the minerals in hydrochloric acid. The values obtained for the heat of combination, $\text{CaO sol.} + \text{CO}_2 \text{ gas} = \text{CaCO}_3 \text{ sol.}$, were, with Iceland spar +21.03 Cal., white, opaque calcite +20.96 Cal., fibrous aragonite +21.26 Cal., and crystallised aragonite +21.33 Cal. The mean value for the heat of conversion of aragonite into calcite is -0.3 Cal., instead of the value +2 Cal., adopted hitherto.

Since aragonite has a higher specific gravity and a higher heat of formation than calcite, its zone of stability should necessarily correspond, as in the case of quartz and the diamond, with lower temperatures and higher pressures than those which correspond with their reversible transformation. C. H. B.

Heat of Dissociation of some Acids. By E. PETERSEN (*Zeit. physikal. Chem.*, 11, 174—184).—The author points out that the heat of dissociation of an acid may be calculated from the heat of dilution, as the latter should be equal to the change in the amount of dissociation on dilution multiplied by the heat of dissociation. A comparison between the heats of dilution of a number of acids, calculated by the above method and directly determined, shows that, allowing for the necessarily large errors of experiment, there is a general agreement between the two. The heat of dissociation may also be calculated from the heat developed in the action of acids on their sodium salts. According to Arrhenius' theory of isohydric solutions, a change in the amount of the dissociation of the acid takes place in this case, which may be calculated by the law of mass action. This change, multiplied by the heat of dissociation of the acid, should be equal to the heat developed on mixing the acid and its sodium salt. In most cases, the heat evolved is too small for direct determination, but the author has been able to verify the theory in two cases, those of hydrogen and sodium fluoride, and of phosphoric acid and sodium dihydrogen phosphate. The observed and calculated values are in fair agreement. H. C.

Behaviour of Colloïds in Organic Solvents (Organosols) at the Critical Temperature of the Solvent. By E. A. SCHNEIDER (*Zeit. anorg. Chem.*, 3, 78—79).—A colloïdal solution of silver in ethyl alcohol (organosol, $\text{Ag}[\text{EtOH}]$), was prepared by dialysing the purified hydrosol into absolute alcohol. It was then heated in sealed

tubes to 250—255° (in the vapour of boiling amyl benzoate), that is, 20° above the critical temperature of ethyl alcohol. The silver coagulated to a reddish-brown mass, and did not redissolve when the alcohol was cooled.

C. F. B.

Graphical Deductions from the Solution Isotherms of a Double Salt and its Components. By F. A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, **11**, 75—109).—The author (*Zeit. physikal. Chem.*, **9**, 57) has given a graphic method for representing the behaviour of a system consisting of three substances, and in this paper describes how it may be applied to the case of a double salt and its two components, showing how the system behaves for variations of temperature, and of the proportion of the substances present.

J. W.

Applications of Beckmann's Boiling Point Apparatus. By M. ROLOFF (*Zeit. physikal. Chem.*, **11**, 7—27).—By means of Beckmann's apparatus, the author has made a series of determinations of the boiling points of aqueous solutions of potassium chloride, varying in concentration from 0.5 to 18.5 grams of salt in 100 grams of water. His results agree fairly well with those formerly obtained by Tammann and Dieterici. He gives a table showing the relation between the elevation of the boiling point of aqueous solutions and their osmotic pressure. Solutions of volatile substances (acetic, formic, nitric, and hydrochloric acids) were also investigated, with results in accordance with the theory as developed by Nernst (*Zeit. physikal. Chem.*, **8**, 110). Nernst has shown theoretically (*Zeit. physikal. Chem.*, **11**, 1) that the reciprocal of the molecular elevation of the boiling point of a homogeneous mixed solvent is composed, according to the simple mixing formula, of the reciprocals of the molecular elevations of the two components and the percentage composition of the mixture. From solutions of naphthalene in a mixture of benzene and chloroform, and of boric acid in mixtures of water and acetic acid, the author obtained numbers in confirmation of this theoretical deduction. Solutions of potassium chloride in water and acetic acid showed that the elevation is nearly independent of the quantity of acetic acid present (in which the salt is insoluble).

An arrangement is described and figured by means of which boiling point determinations may be made at any desired constant pressure.

J. W.

Measurements of Van der Waals' Surface for Mixtures of Carbonic Anhydride and Methylic Chloride. By J. P. KUENEN (*Zeit. physikal. Chem.*, **11**, 38—48).—The author has investigated various mixtures of carbonic anhydride and methylic chloride with respect to their pressure, volume, and temperature, in order to test the validity of Van der Waals' theory (*Zeit. physikal. Chem.*, **5**, 133) as applied to mixtures. He employed a Ducretet compression apparatus, and found it necessary to use a small piece of iron rod, set in motion within the experimental tube by means of an electromagnet, in order to hasten the attainment of equilibrium. Van der Waals' theoretical deductions were in general confirmed. There exists for each mixture

a temperature, called by the author the critical contact point, which corresponds with the critical point of a pure substance. The phenomenon of retrograde condensation was observed; that is, for a mixture, the quantity of liquid at first increases on compression, then reaches a maximum, and finally diminishes to the vanishing point. At the temperatures and pressures of experiment, no indication of the co-existence of three phases was observed. J. W.

Determination of the Molecular Weight from the Rate of Evaporation. By H. KRONBERG (*Monatsh.*, 14, 24—27).—If a non-volatile substance is dissolved in a fairly volatile liquid, the rate of evaporation of the latter is decreased. This may be considered as due to the fact that, with the solution, the surface exposed consists partly of the volatile molecules of the solvent and partly of the non-volatile molecules of the dissolved substance, and not, as when the solvent alone is exposed, solely of volatile molecules. The greater the number of non-volatile molecules the less the evaporation, or, in other words, the rate of evaporation of such a solution as the above will decrease regularly with the concentration, and will be inversely proportional to the molecular weight of the dissolved substance. The molecular weight of any compound might, therefore, be determined from the rate of evaporation of one of its solutions, just as from the reduction of the freezing point.

To carry out a determination, weighed quantities of two solutions, one of a substance of known, and the other of the substance of unknown, molecular weight, in the same solvent, should be exposed either in the open air or in a vacuum for some length of time, and then re-weighed. The losses in each case, calculated for 100 parts of the pure solvent, will be inversely proportional to the molecular weights of the dissolved substances, and since one of these is known, the other can then be ascertained. H. C.

A more Exact Cryoscopic Method. By E. H. LOOMIS (*Ber.*, 26, 797—801).—The apparatus consists of two thin-walled test-tubes placed one within the other, and joined at the upper ends by a piece of india-rubber tubing, the annular space between them being about 1 mm. in thickness. The inner test-tube measures 28×3 cm., and its bottom is drawn in to prevent the formation of compact pieces of ice upon it; an india-rubber ring placed round it prevents it from touching the outer test-tube. Through its cork passes a thermometer, the scale-divisions (0.01°) of which are 0.4 mm. long, and a stirrer, consisting of a glass rod with a platinum ring; to the outer side of which a bit of a feather is so attached as to sweep the walls of the test-tube and prevent the formation of ice upon them. The temperature is read to 0.0001 with a microscope and eye-piece micrometer, 10 of whose divisions are equivalent to 1 of the thermometer's; during the reading, the thermometer is continually tapped by a small electric hammer. Three baths are used: a "main bath," consisting of a copper cylinder, 35×6 cm., thickly surrounded with felt, and containing a freezing mixture at 0.3° below the melting point to be determined; a "freezing bath" at -10° ; and a "melting bath" at

0°. The process is as follows:—Some ice is formed in the apparatus, and the latter is then brought into the melting bath until the ice has nearly disappeared. It is now placed in the freezing bath; the temperature falls to 0.1—0.2° below the freezing point of the mixture, and the water then begins to freeze. The apparatus is immediately transferred to the main bath, the hammer set in motion, and the temperature read after the lapse of two minutes. It is then again brought into the melting bath until the ice has nearly disappeared, and the process repeated 6—10 times as above; successive readings rarely differ by 0.001°. Solutions of the following substances were examined; the numbers represent the extreme values of the molecular depression (lowering of freezing point ÷ gram-molecules per litre), the corresponding number of gram-molecules per litre being 0.01—0.20; except in the case of alcohol, where it was 0.01—0.16; sodium chloride, 3.67—3.44°; cane sugar, 1.71—1.96°; magnesium sulphate, 2.65—2.08°; alcohol; 1.72—1.83°; sulphuric acid, 4.49—3.85°; phosphoric acid, 2.31—1.79°, carbamide, 1.72—1.83°. The rise or fall of the molecular depression with increasing concentration is, in all the cases examined, a continuous one.

C. F. B.

Freezing Points of Sulphuric acid of Different Concentrations, and the Sulphuric acid contained in the Solid and Liquid Portions. By J. THILO (*Chem. Zeit.*, 16, 1688—1689).—The author has determined the freezing points of sulphuric acid of different concentrations and gives his results in the following table.

Formula.	Per cent. H ₂ SO ₄ .	Sp. gr.	Freezing point.
H ₂ SO ₄	100.0	1.842	+10.5°
	95.2	1.834	—24.5
	89.17	1.815	—47.0
	88.88	1.813	—55.0
H ₂ SO ₄ ,H ₂ O	84.48	1.777	+ 3.5
	83.82	1.772	+ 4.5
	83.74	1.771	+ 5.0
	83.00	1.765	+ 8.0
	80.84	1.743	+ 2.5
	80.09	1.734	+ 1.5
	77.2	1.701	—14.0
	74.85	1.673	—41.0
H ₂ SO ₄ ,2H ₂ O	73.08	1.650	—70.0
H ₂ SO ₄ ,4H ₂ O	57.65	1.476	—40.0
H ₂ SO ₄ ,6H ₂ O	47.57	1.376	—50.0
H ₂ SO ₄ ,8H ₂ O	40.50	1.311	—65.0
H ₂ SO ₄ ,10H ₂ O	35.25	1.268	—88.0
H ₂ SO ₄ ,11H ₂ O	33.11	1.249	—75.0
H ₂ SO ₄ ,12H ₂ O	31.21	1.233	—55.0
H ₂ SO ₄ ,13H ₂ O	29.52	1.219	—45.0
H ₂ SO ₄ ,14H ₂ O	28.0	1.207	—40.0
H ₂ SO ₄ ,15H ₂ O	26.63	1.196	—34.0
H ₂ SO ₄ ,16H ₂ O	25.39	1.187	—26.5
H ₂ SO ₄ ,18H ₂ O	23.22	1.170	—19.0
H ₂ SO ₄ ,20H ₂ O	21.40	1.157	—17.0
H ₂ SO ₄ ,25H ₂ O	17.88	1.129	— 8.5

Formula.	Per cent. H_2SO_4 .	Sp. gr.	Freezing point.
$\text{H}_2\text{SO}_4, 30\text{H}_2\text{O}$	15·36	1·109	— 6·5°
$\text{H}_2\text{SO}_4, 40\text{H}_2\text{O}$	11·98	1·084	— 4·5
$\text{H}_2\text{SO}_4, 50\text{H}_2\text{O}$	9·82	1·067	— 3·5
$\text{H}_2\text{SO}_4, 75\text{H}_2\text{O}$	6·77	1·045	0·0
$\text{H}_2\text{SO}_4, 100\text{H}_2\text{O}$	5·16	1·032	+ 2·5
$\text{H}_2\text{SO}_4, 150\text{H}_2\text{O}$	3·5	1·020	+ 3·0
$\text{H}_2\text{SO}_4, 200\text{H}_2\text{O}$	2·65	1·013	+ 4·0
$\text{H}_2\text{SO}_4, 300\text{H}_2\text{O}$	1·78	1·007	+ 4·5
$\text{H}_2\text{SO}_4, 320\text{H}_2\text{O}$	1·67	1·006	+ 3·5
$\text{H}_2\text{SO}_4, 340\text{H}_2\text{O}$	1·58	1·006	+ 2·5
$\text{H}_2\text{SO}_4, 360\text{H}_2\text{O}$	1·50	1·005	+ 1·5
$\text{H}_2\text{SO}_4, 400\text{H}_2\text{O}$	1·34	1·005	+ 1·0
$\text{H}_2\text{SO}_4, 1000\text{H}_2\text{O}$	0·54	1·001	— 0·5

These results give a very irregular curve, crossing the line of zero temperature in five different places.

In most cases, the frozen portion of the acid was separated from that which still remained liquid, and each separately analysed. The percentage of sulphuric acid in the two portions was seldom found to be the same, and only generally where the freezing point curve attains a maximum or a minimum. In other cases the liquid portion contained the larger quantity of sulphuric acid.

H. C.

Note by Abstractor.—In the above paper, the author makes no reference to previous determinations. The majority of his results differ considerably from those of Pickering (*Trans.*, 1890, 331), and the assigned *rise* in the freezing point of water on the addition of 1—6 per cent. H_2SO_4 , which is out of keeping with the general cryoscopic behaviour of aqueous solutions, must be regarded as very doubtful.

H. C.

Freezing Point of very Dilute Solutions. By H. C. JONES (*Zeit. physikal. Chem.*, 11, 110—116, and *Ber.*, 26, 547—553).—By using a large quantity of solution (1 litre), a thermometer divided into thousandths of a degree, and having the experimental vessel surrounded by a jacket of stagnant air, the author has succeeded in obtaining numbers for the lowering of the freezing point in very dilute aqueous solutions differing at most by 0·0004°. The correction for the increase in the concentration of the solution, due to the separation of ice, was in all cases applied. The substances investigated were sodium, potassium, and ammonium chlorides. All these salts give continuous curves (almost straight lines) for the lowering of the freezing point, without any of the breaks observed by Pickering.

The following table gives the percentage difference between the results of the two observers for solutions of sodium chloride.

Gram-molecules per litre.	Difference.
0·01	4·0 per cent.
0·005	10·7 "
0·002	11·4 "
0·001	53·8 "

J. W.

Mixtures of Ether and Water. By L. MARCHIS (*Compt. rend.*, 116, 388—390).—The author shows that the vapour tension of a mixture of ether and water is independent of the composition of the mixture, and equal to that of anhydrous ether, whether the water added is so small in quantity that it all dissolves in the ether or so large that the solution separates into two layers. H. C.

Determination of the Specific Gravity of Liquids for Practical Purposes. By C. R. A. WRIGHT (*J. Soc. Chem. Ind.*, 11, 297—305).—The author discusses in detail the appliances ordinarily used for determining the sp. gr. of a given liquid; in cases in which a high degree of accuracy is requisite, he has found certain modifications of the existing instruments of considerable practical use. He describes a modified form of pycnometer which he has found very serviceable, not only in obtaining values exact to five places of figures if requisite, but also in obtaining a series of valuations at different temperatures with comparatively little trouble. Various useful tables for correction are also given. D. B.

Specific Gravity Apparatus. By H. B. FULTON (*J. Soc. Chem. Ind.*, 11, 305—306).—The apparatus consists of a glass tube, having as uniform a diameter as possible, graduated from zero upwards and weighted with mercury so as to maintain a vertical position when floated in water. The neck by which the mercury bulb is attached is comparatively a long one, so that the centre of gravity may be as low as possible. The lower part of the tube is blown so as to have a small, flattened, protruding bulb to act as a fender and thus insure more accurate readings by preventing the tube from clinging to the sides of the test jar. Water is first poured into the tube to fill it at least to zero on the scale; a little more does not matter, and there should be sufficient to completely cover the sample under examination. Supposing it to have been filled exactly to zero, the tube is then floated in a jar of water and the level at which it floats is read off. This may be, say, 20. The sample is now dropped into the tube, which at once sinks, say, to 55, and the weight of the sample is thus ascertained as $55 - 20 = 35$. At the same time, however, the volume is obtained by noting the displacement of the water inside the tube, and again assuming this reading to be 5, we have at once sp. gr. $= 35/5 = 7$. D. B.

The Molecular Volumes of Dissolved Alkali Salts and their Relation to the Atomic Volumes of the Elements. By J. TRAUBE (*Zeit. anorg. Chem.*, 3, 11—33; compare Abstr., 1892, 1383).—A not very coherent paper, containing calculations of the molecular volumes of a large number of alkali salts in aqueous solutions of varying concentration, together with a somewhat desultory discussion of the results obtained. The coefficient of electrolytic dissociation is known to increase with dilution of the solution; the molecular volume, on the other hand, decreases, but apparently also tends to a fixed limit. A further relation between the two appears from the fact that, when compounds are compared by pairs—either those of

a base with two different acids, or those of an acid with two different bases—in solutions of varying concentration, the difference between the molecular volumes, at any given concentration, of the two members of a pair remains constant as the concentration varies, if the ratio of the coefficients of electrolytic dissociation of these substances also remains constant; in the opposite case, it also varies. Further, in many cases the difference in molecular volume between the salts of one and the same base with two similarly constituted acids varies considerably with the base. Yet another point is, that salts which are anhydrous, or which do not crystallise with more than $3\text{H}_2\text{O}$, have, in concentrated solutions, nearly the same molecular volume as in the solid state; this is not the case with salts that crystallise with more than $3\text{H}_2\text{O}$, but the difference vanishes, or is much reduced, if the salt in solution is regarded as still combined with its water of crystallisation. The fact that this water of crystallisation occupies a less volume than in the free state is accounted for by supposing free water to consist of complex molecules, and the transformation of this water into water of crystallisation to be accompanied by a breaking up of these complex molecules, and a consequent decrease of molecular volume. Finally, the following proposition is enunciated:—The atomic volumes of hydrogen, lithium, and sodium are equal, that of rubidium is nearly equal to that of ammonium, and the atomic volume increases from Na : K : Rb : Cs by a difference which is apparently nearly constant, and has a mean value of 10 units of molecular volume.

C. F. B.

Dissociation of Salts into their Ions by Water of Crystallisation. By C. E. LINEBARGER (*Amer. Chem. J.*, 14, 604—606).—In the case of a solution of copper sulphate which contains Cu ions, SO_4 ions, and undissociated CuSO_4 molecules, the colour must be due to the copper ions, for the SO_4 ions are colourless, and so is the anhydrous molecule of copper sulphate. The colour of the salt crystallised with water of crystallisation must, then, also be due to the presence of free copper ions, or, in other words, *water of crystallisation has the power of dissociating crystallised salts into their ions.* By analogy, this will be true also in the case of colourless salts.

C. F. B.

Deviations from the Gaseous Laws in Solutions. By S. J. THUGUTT (*Ber.*, 26, 583—589).—Deviations from the gaseous laws in aqueous solutions may be explained, according to the author, by assuming that hydrolytic, as well as electrolytic, dissociation takes place in the dilute solutions, and that the formation of hydrates occurs in concentrated solutions.

H. C.

Diffusion in Aqueous Salt Solutions. By R. ABEGG (*Zeit. physikal. Chem.*, 11, 248—264).—The diffusion experiments described in this paper were carried out with apparatus similar to that used by Arrhenius in his investigations on diffusion in salt solutions (*Abstr.*, 1892, 1265). The diffusing substance was in the first case ammonia, and in the second acetic acid, alcohol being also used in later determinations. All solutions were of normal concentration. The diffu-

sion coefficients were divided by that for water alone, the relative rates of diffusion of ammonia and acetic acid in various salt solutions being in this way referred to those of pure water. The values obtained for ammonia were found generally to be in the order of the fluidities of the salt solutions, but this was not the case with acetic acid. This was found to be due to the fact that acetic acid in most cases alters the osmotic pressure of the salt solution into which it diffuses, and, therefore, the diffusion does not pursue a regular course. Where this alteration in osmotic pressure does not occur, it may be generally stated that the fluidity of water is altered in the same manner, although to a greater degree, by the addition of a salt, as is its resistance to the passage of diffusing molecules. H. C.

Explanation of Affinity. By H. SACHSE (*Zeit. physikal. Chem.*, 11, 185—219).—The author endeavours to deduce a number of the chemical properties of the elements and their compounds from the hypotheses that atoms possess polarity, and that the general mass attraction may become a repulsion if the distance between the centres of gravity is smaller than a certain value. H. C.

The Decomposition of Silver Chloracetate. By J. H. KASTLE (*Amer. Chem. J.*, 14, 586—597).—This was at first studied by placing 0.2015 gram of the salt in a sealed tube with 500 times the amount of water necessary for its complete decomposition, heating the tube in a bath kept at a temperature of 134—135°, removing it, allowing it to cool for 10 minutes, opening it, and determining the amount of undecomposed silver salt by titration with ammonium thiocyanate. The products of decomposition are, of course, silver chloride and glycollic acid. The rate of decomposition was found to rise rapidly until it reached a maximum at the end of 13 minutes, after which it decreased, rapidly at first, afterwards more slowly; at the end of two hours, the decomposition was practically complete. The initial rise was evidently due to the fact of a rise in temperature, for the tube did not acquire the temperature of the bath until after the lapse of 20 minutes. But why should there be a subsequent *fall* in the rate of decomposition, setting in even before the tube had attained its maximum temperature? Special experiments showed that the silver chloride formed had no, and the glycollic acid but little, retarding effect; it was found, however, that the amount of decomposition in the same time is very much less as the amount of water, relatively to that of the silver chloracetate, is greater. The explanation of the decrease in rate of decomposition in the original series of experiments is, therefore, that as the decomposition of the silver chloracetate progresses, the amount of water present becomes larger and larger, relatively to that of the salt left undecomposed, and consequently the rate of decomposition diminishes. As for the retarding effect that increase in the relative amount of water exercises, it may be explained thus. The silver in the chloracetate is converted into a chloride; we have thus, as it were, chloracetic acid striving with (potentially formed) hydrochloric acid for the possession of the silver, and the less the affinity of the latter acid for the silver, the less rapid will be

the decomposition. Now Ostwald has shown that the affinity of chloracetic acid increases rapidly with increasing dilution, whilst that of hydrochloric acid undergoes but a very slight increase; hence the effect of the addition of water is to diminish the affinity of the hydrochloric acid for the silver, relatively to that of the chloracetic acid, and, consequently, to diminish the rate of decomposition of the silver salt.

C. F. B.

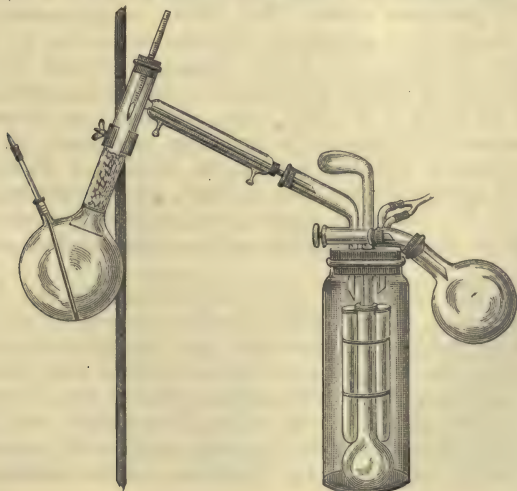
Periodic Law. By G. C. SCHMIDT (*Monatsh.*, **14**, 8—23).—The atomic volumes, melting points, and coefficients of expansion by heat of the elements are periodic functions of the atomic weights. Since each of the above properties may be assumed to depend on the number of atoms present in the solid molecule of each of the elements, it follows generally that the molecular masses of the elements are periodic functions of their atomic weight.

H. C.

New System of Atomic Weights, partly based on the Direct Determination of the Molecular Weights. By A. LEDUC (*Compt. rend.*, **116**, 383—386).—The system of atomic weights at present in use is in part based on the determinations of the composition of potassium chlorate, which, as Hinrichs has recently shown (this vol., ii, 163), are open to grave doubt. These atomic weights also lead to very different molecular volumes for gases which resemble one another closely in physical properties, and they do not coincide with the electrochemical equivalents. It therefore appears desirable that a new system of atomic weights should be built up, making use of direct determinations of gaseous density and of electrochemical equivalents. The author gives a list of some atomic and molecular weights determined in this manner.

H. C.

New Apparatus. By A. MICHAEL (*J. pr. Chem.* [2], **47**, 197—199).—The distillation apparatus figured below explains itself to a



great extent. The Hempel beads are contained in the neck of the flask, in order to avoid the usual prolonged column and the employment of a second cork. This necessitates a subsidiary neck in the flask for the Wurtz's air-tube. The tube which delivers into the reception chamber is provided with a three-way cock which will allow of air being let into the flask without disturbing the vacuum in the chamber; or, as here depicted, a flask may be attached to it for the collection of the largest fraction which could not be contained in the reception chamber tubes. The Y-tube, leading to the water pump, enables a vacuum to be maintained in the whole apparatus.

A slight variation on the usual form of apparatus for the determination of melting points, and a hot jacket for a funnel are also figured; the latter is provided with an inlet and an outlet tube which can either be connected with a boiler and condenser respectively, or with a hot water supply.

A. G. B.

Hydrogen Sulphide Apparatus. By H. TREY (*Zeit. anal. Chem.*, **31**, 667—669).—In the *Zeit. anal. Chem.*, **31**, 183, Ostwald described a constant hydrogen sulphide apparatus, set up for the use of a students' laboratory. To prevent waste of the gas, the whole apparatus is enclosed in a box, so that nothing is accessible except a projecting brass tube, and the button of a pinch-cock, which latter, except when pressed, closes a rubber tube connecting the brass nozzle with the gas generator.

M. J. S.

Inorganic Chemistry.

Amide and Imide of Sulphuric Acid. By W. TRAUBE (*Ber.*, **26**, 607—613 (compare Abstr., 1892, 1389)).—Sulphamide and sulphimide are formed when sulphuryl chloride is treated with ammonia in chloroform solution, the action being expressed by the equations—(1) $\text{SO}_2\text{Cl}_2 + 4\text{NH}_3 = 2\text{NH}_4\text{Cl} + \text{SO}_2(\text{NH}_2)_2$ and (2) $\text{SO}_2\text{Cl}_2 + 3\text{NH}_3 = 2\text{NH}_4\text{Cl} + \text{SO}_2\text{:NH}$. In addition to these products, Mente's imidosulphurylamide is probably produced, in accordance with the equation $2\text{SO}_2\text{Cl}_2 + 7\text{NH}_3 = 4\text{NH}_4\text{Cl} + \text{NH}(\text{SO}_2\text{:NH}_2)_2$; although this substance was not isolated, its formation seems to be established by the fact that ammonium imidosulphonate was invariably present in the solution obtained on treating the product with water.

Sulphamide can be isolated in the following manner. Well-cooled sulphuryl chloride, diluted with 15—20 volumes of chloroform, is saturated with anhydrous ammonia, the precipitated product dissolved in water, the solution acidified with nitric acid, and the whole of the chlorine precipitated with silver nitrate; the filtered solution is neutralised with alkali, treated with silver nitrate, and the crystalline precipitate, which consists of silver sulphimide and some other silver derivative, separated by filtration. After adding a further

quantity of silver nitrate, the clear solution is treated with alkali, when silver sulphamide is obtained as a colourless, amorphous precipitate, which, however, is invariably mixed with some other silver compound, probably the same as that present in the silver sulphimide precipitate. In order to remove this impurity, the well-washed precipitate is treated with hydrochloric acid in quantity exactly sufficient to convert the silver into chloride, and the strongly acid solution is neutralised with ammonia and mixed with silver nitrate, when only the silver compound of unknown composition is precipitated; pure silver sulphamide can now be precipitated by adding silver nitrate and excess of ammonia, and on decomposing this compound with the necessary quantity of hydrochloric acid, a neutral or feebly acid solution of sulphamide is obtained.

Sulphamide is deposited in large, colourless crystals when its aqueous solution is evaporated over sulphuric acid under reduced pressure; it sinters at 75° , melts at 81° , and begins to lose ammonia at slightly higher temperatures, decomposing completely, with evolution of acid vapours, when heated above 250° . It is very readily soluble in water, its aqueous solution having a neutral reaction and a bitter taste, but it is insoluble in alcohol, ether, and other organic liquids. It is decomposed into sulphuric acid and ammonia by boiling acids, but when treated with alkalis, it is converted into sulphamic acid; it is decomposed by nitrous acid in the cold, with formation of sulphuric acid.

The *silver* derivative, $\text{SO}_2(\text{NHAg})_2$, prepared by digesting sulphamide with ammonia and excess of silver nitrate, is a colourless, amorphous powder, only slightly sensitive to light; it has an alkaline reaction, and dissolves freely in nitric acid and ammonium carbonate, but is only sparingly soluble in cold water. It loses ammonia when heated, and decomposes completely at about 200° with evolution of sulphurous anhydride; it reacts with alkylic iodides and with acid chlorides, and its aqueous solution gives precipitates with mercuric nitrate and lead acetate.

Sulphimide, $\text{SO}_2\text{:NH}$, is formed, together with ammonia and imido-sulphonic acid, when sulphamide is heated at $200\text{--}210^{\circ}$; the solid product is treated with water, the solution mixed with silver nitrate, and the precipitated silver sulphimide (*loc. cit.*) purified by recrystallisation; on decomposing the pure substance with the necessary quantity of dilute hydrochloric acid, an aqueous solution of sulphimide is obtained. This solution has a strongly acid reaction, decomposes carbonates, and, when not too concentrated, can be boiled for a short time without decomposition of the imide taking place; on evaporation even at a temperature below 40° , ammonium hydrogen sulphate remains, so that the sulphimide could not be obtained in crystals. Sulphimide is rather rapidly decomposed by warm acids, yielding sulphuric acid and ammonia, but it is only slowly acted on by excess of alkalis even on boiling. *Potassium sulphimide*, $\text{SO}_2\text{:NK}$, prepared by treating the silver derivative with a hot solution of the theoretical quantity of potassium chloride, forms well-defined, colourless crystals, and is not extremely soluble in water; its solution has a neutral reaction and is very stable, but is slowly decomposed by

boiling acids; the dry substance decomposes when heated, glowing vividly, and leaving a residue of potassium sulphate and sulphite, nitrogen and sulphurous anhydride being evolved. The *sodium* derivative, $\text{SO}_2\cdot\text{NNa}$, is a crystalline powder, very readily soluble in water, and, like the potassium derivative, very stable. The *ammonium* derivative, $\text{SO}_2\cdot\text{N}\cdot\text{NH}_4$, crystallises in colourless needles, and is readily soluble in water, but insoluble in alcohol; when quickly heated, it is partially converted into sulphamide, but when heated slowly, it first gives off ammonia, and then melts at about 250° with complete decomposition. The *calcium* derivative is readily soluble in water, and difficult to obtain in crystals. The *barium* derivative, $(\text{SO}_2\cdot\text{N})_2\text{Ba} + 2\text{H}_2\text{O}$, crystallises in lustrous needles, loses its water when carefully heated, dissolves freely in water, and is decomposed by boiling hydrochloric acid, barium sulphate being formed; in its aqueous solution, silver nitrate produces a very sparingly soluble precipitate. The *lead* derivative crystallises from hot dilute alcohol in long needles; the copper derivative is a green, amorphous powder.

F. S. K.

Electrical Properties of Pure Substances. I. The Preparation of Pure Nitrogen and attempts to condense it. By R. THRELFALL (*Phil. Mag.* [5], 35, 1—35).—The author has examined the processes recommended by various workers for the preparation of pure nitrogen. The method depending on the absorption of oxygen by passing air over heated copper is the most frequently mentioned; it is, however, a very objectionable one. The formation of oxides of nitrogen, the difficulty of making connection with the heated porcelain tube, and the possibility of the latter being permeable to hot furnace gases, together with the chance of a minute crack occurring in the tube and escaping detection, are amongst the mechanical disadvantages of the process. The preparation of the very pure hydrogen or carbonic oxide necessary for reducing the copper oxide presents great difficulty; if the copper absorbs sulphur, some of the latter is liable to burn out during many subsequent oxidations, and the sulphurous anhydride so formed becomes troublesome, inasmuch as no suitable reagent is known which really retains this gas. The preparation of pure nitrogen by passing air over heated phosphorus is troublesome, and there is no guarantee that the potassium permanganate, used to absorb phosphorus vapour from the resulting gas, is really efficacious; Warburg had to electrolyse the glass of his vacuum tubes in order that the nascent sodium so formed should remove the last traces of oxygen and hydrogen from the nitrogen prepared by this method, which is hence an undesirable one. Ammonium dichromate was prepared from the purest materials, and purified with the greatest care; the nitrogen obtained on heating it, however, contained nitrous compounds, for which no satisfactory absorbent is known.

The author finally adopted the method of absorbing the oxygen from air by means of copper and ammonia, the last traces of oxygen being removed by chromous chloride; the latter substance was prepared by Recoura's method (*Abstr.*, 1886, 669), the blue solution being evaporated to a clear syrup under reduced pressure in an

atmosphere of carbonic anhydride. The gas was purified in a glass apparatus, consisting of a series of vessels containing the substances necessary for removing impurities; indiarubber was excluded, all the joints were hermetically sealed, and the glass taps ground with extreme care and sealed with mercury. The absorbing vessels used for the complete purification of the nitrogen obtained by treating dust-free air with copper and ammonia were the following:—A wash bottle containing concentrated sulphuric acid, two wash bottles and a U-tube of chromous chloride syrup, a tube of caustic potash, a tube containing silver nitrate solution with a little moist silver oxide and potassium nitrate, a tube each of potash and sulphuric acid, a U-tube containing solid potash and soda-lime in the two limbs, a bottle and three tubes exposing a large surface of phosphoric anhydride, and finally three tubes containing sulphur, silver, and copper respectively. All the substances used in the preparation were themselves carefully purified by methods which are fully discussed in the paper. The author remarks that all the samples of potash and soda examined by him, including potash obtained by exposing clean potassium to moist air, yielded traces of nitrites when dissolved. The phosphoric anhydride employed was prepared by burning phosphorus in a strong current of air; the anhydride could only be completely freed from phosphorus by distillation in a rapid stream of oxygen, which, for this purpose, was prepared in a state of great purity.

The spectrum of the nitrogen, purified in this way, was examined in a tube fitted with external electrodes. The band spectrum did not show any of the characteristic hydrocarbon or hydrogen lines; the absence of these latter gases was hence assured.

Thomson and Threlfall (Abstr., 1887, 328) observed that on passing an electric discharge through pure nitrogen the pressure diminishes; this, if due to molecular condensation of the gas, would be of considerable importance. The author therefore made a large series of experiments in order to obtain a repetition of the phenomenon; it was found, however, that the decrease of pressure was due to the formation of a nitride of mercury, probably identical with Plantamour's trimercuramine (*Annalen*, **40**, 115), by the action of the discharge on the mercury in the gauge. The compound is formed as a brown film on the glass when the electric discharge is passed over a mixture of nitrogen and mercury at about 8 mm. pressure; seven-eighths or so of the nitrogen present may be absorbed with formation of this substance, which decomposes at about 200°, and behaves as a dissociable compound on heating and cooling. It can, however, be entirely decomposed by repeated heating and cooling. No real condensation of the gas, owing to an increase in the molecular weight, can be induced at -10° under a pressure of 8 mm. The appearance of the spark discharge in pure nitrogen can be changed by slight variations of temperature and, possibly, of E.M.F.; no explanation of these changes can at present be given. W. J. P.

Preparation of Nitric Oxide. By C. M. VAN DEVENTER (*Ber.*, **26**, 589—593).—See this vol., ii, 298.

Density of Nitric Oxide. By A LEDUC (*Compt. rend.*, 116, 322—323).—Nitric oxide expelled from solutions of ferrous salts at a temperature not exceeding 40° to 50° is not completely absorbed by treatment with similar solutions. The insoluble residue amounts to 0.1 per cent., and is increased if the temperature at which the gas is expelled from the liquid is as high as 90°; it rekindles a glowing splint. Making the necessary correction, the density of nitric oxide becomes 1.0387, with a probable error of not more than a unit in the fourth decimal place. If the atomic weight of nitrogen is taken as 13.97, the ratio of the molecular volume of nitric oxide to that of oxygen is 0.99987, which seems to agree well with the critical points of the two gases. C. H. B.

Reduction of Nitric acid by Copper. By P. C. FREER and G. O. HIGLEY (*Amer. Chem J.*, 15, 71—81).—The pure copper having been introduced into a flask, all air is expelled by carbonic anhydride, the flask is heated to the desired temperature, and the nitric acid, heated to the same temperature, is run in. Agitation is maintained until solution is complete, when all gases are swept forward by carbonic anhydride; nitrous anhydride and nitric peroxide are absorbed by sulphuric acid; both form nitrosylsulphuric acid, but in the case of the nitric peroxide only half the nitrogen is converted into this compound, the rest appearing as nitric acid; it is thus possible, by titrating one portion of the sulphuric acid with permanganate, after Lunge (this Journal, 1877, ii, 642), and making a total nitrogen determination on the other portion in a nitrometer, to estimate the quantity of these two nitrogen oxides. The nitrous oxide, nitric oxide, and nitrogen are collected in a eudiometer, and the nitric oxide determined by addition of oxygen, and the nitrous oxide by explosion with hydrogen.

The authors arrive at the following conclusions at this stage of their investigation:—(1) The sole products of reduction of excess of nitric acid (sp. gr. 1.40) by copper are nitrous anhydride and nitric peroxide, the proportion being about 10 per cent. of the former to 90 per cent. of the latter; (2) the effect of varying temperature on the proportion of the reduction products is, apparently, but slight. They discuss these conclusions in the light of Montemartini's papers on the action of nitric acid on metals (*Abstr.*, 1892, 1278, 1279).

A. G. B.

Amidophosphoric acid. By H. N. STOKES (*Amer. Chem. J.*, 15, 198—214).—See this vol., i, 316.

Preparation of Pure Phosphoric acid from Sodium Phosphate, and by the Phosphorus-Nitric acid Method. By G. WATSON (*J. Soc. Chem. Ind.*, 11, 224—228).—Crystals of hydrogen sodium phosphate were subjected to the action of gaseous hydrogen chloride. In this manner, syrupy phosphoric acid, in amount corresponding with a yield of 75 per cent. of the theoretical quantity, was obtained. From the results of further trials, the author was inclined to believe that a considerable portion of the hydrogen sodium phosphate was not decom-

posed, but was simply thrown down as sodium phosphate. He then investigated the reaction more closely, using anhydrous sodium pyrophosphate instead of crystallised hydrogen sodium phosphate, and digesting it with definite weights of pure aqueous hydrochloric acid. The hydrochloric acid acts with two functions: firstly, a portion is used to saturate half the alkali in the pyrophosphate, then the remainder acts on the resulting salt, and sets free twice its weight of orthophosphoric acid. The following equation represents the final distribution of matter when equivalent quantities of sodium pyrophosphate and aqueous hydrochloric acid are digested together at the ordinary temperature:— $\text{Na}_4\text{P}_2\text{O}_7 + 4\text{HCl} + \text{Aq} = 3.49 \text{NaCl} + 1.49\text{H}_3\text{PO}_4 + 0.51\text{HCl} + 0.51\text{NaH}_2\text{PO}_4$, whilst the expression representing the complete decomposition of the pyrophosphate by the minimum of hydrochloric acid is $\text{Na}_4\text{P}_2\text{O}_7 + 4.685\text{HCl} + \text{Aq} = 2\text{H}_3\text{PO}_4 + 4\text{NaCl} + 0.685\text{HCl} + \text{Aq}$. This reaction was not found to constitute a paying process for the manufacture of phosphoric acid.

It is known that on dissolving yellow phosphorus in dilute nitric acid a certain amount of phosphorous acid is produced, which amount is greater at the initial stages of the solution, and the author has attempted to determine the relative proportions of the two acids. His experiments seem to show that as the strength of the nitric acid is reduced, the ratio of the phosphorous to the phosphoric acid alters until it corresponds with that of equal weights. In the first trials, in which the strongest acids were used, it was found that reducing the time of cohobation also increased the proportion of phosphorous acid. These trials show that, in addition to the fundamental reaction, a secondary one is going on, in which the phosphorous acid formed in the primary action is being oxidised to phosphoric acid. The author concludes, from his experiments, that the balance of evidence, so far as it goes, is in favour of the statement that the primary action taking place is one in which equal weights of phosphorous and phosphoric acids are formed. In carrying out this reaction for the preparation of phosphoric acid, the author finds that it is not advisable to use an acid of greater sp. gr. than 1.250, nor one much below 1.200. By increasing the surface of the phosphorus, the speed of the reaction can be safely accelerated to a certain extent. D. B.

Crystalline Arsenates. By C. LEFÈVRE (*Ann. Chim. Phys.* [6], 27, 5—62; compare Abstr., 1890, 562 and 1377).—*Barium pyroarsenate*, $2\text{BaO}, \text{As}_2\text{O}_5$, is formed when barium oxide is added to fused potassium or sodium metarsenate, or to a mixture of one of these salts with less than 40 per cent. of the corresponding chloride; on cooling very slowly, the salt is obtained in colourless, transparent plates, belonging to the orthorhombic system; when treated with cold water, it is quickly converted into the salt of the composition $2\text{BaO}, \text{As}_2\text{O}_5 + 6\text{H}_2\text{O}$. The double salt, $2\text{BaO}, \text{K}_2\text{O}, \text{As}_2\text{O}_5$, is obtained when barium oxide is added to a fused mixture of potassium pyroarsenate and potassium chloride, provided that the latter forms less than 80 per cent. of the mixture; it crystallises in colourless, transparent prisms, which become opaque when treated with cold water. When barium oxide is added to a fused mixture of sodium pyro-

arsenate and sodium chloride containing more than about 18 per cent. of the pyroarsenate, a crystalline salt of the composition $3\text{BaO}, \text{As}_2\text{O}_5$, is produced.

The salts $2\text{SrO}, \text{As}_2\text{O}_5$; $2\text{SrO}, \text{K}_2\text{O}, \text{As}_2\text{O}_5$; $2\text{SrO}, \text{Na}_2\text{O}, \text{As}_2\text{O}_5$; $3\text{SrO}, \text{As}_2\text{O}_5$; $2\text{CaO}, \text{As}_2\text{O}_5$; $2\text{CaO}, \text{K}_2\text{O}, \text{As}_2\text{O}_5$; and $2\text{CaO}, \text{Na}_2\text{O}, \text{As}_2\text{O}_5$ were prepared in a similar manner; they are all crystalline, and, in most cases, are isomorphous with the corresponding barium salts.

The double salt $4\text{CaO}, 2\text{Na}_2\text{O}, 3\text{As}_2\text{O}_5$ is formed when about 5 per cent. of calcium oxide is added to sodium metarsenate fused at a low temperature; it crystallises in large, transparent plates, apparently uniaxial and negative.

Lead pyroarsenate, $2\text{PbO}, \text{As}_2\text{O}_5$, prepared by saturating fused potassium metarsenate with lead oxide, crystallises in colourless plates, which slowly become opaque when treated with water; it is isomorphous with the corresponding salts of the alkali earths. The double salt, $2\text{PbO}, \text{K}_2\text{O}, \text{As}_2\text{O}_5$, is formed when lead oxide is dissolved in a fused mixture of potassium arsenate and potassium chloride, but, unless the arsenate forms more than 25 per cent., chlorine compounds are produced; it crystallises in small, transparent prisms. The corresponding sodium salt, $2\text{PbO}, \text{Na}_2\text{O}, \text{As}_2\text{O}_5$, and the compound $4\text{PbO}, 2\text{Na}_2\text{O}, 3\text{As}_2\text{O}_5$ were prepared.

A double salt of the composition $8\text{CuO}, \text{K}_2\text{O}, 3\text{As}_2\text{O}_5$ is obtained on dissolving about 10 per cent. of cupric oxide in fused potassium metarsenate, but, in presence of a small quantity of potassium chloride, a compound of the composition $2\text{CuO}, \text{K}_2\text{O}, \text{As}_2\text{O}_5$ is formed; they both crystallise in bluish-green prisms, showing oblique extinction.

The sodium salts, $2\text{CuO}, \text{Na}_2\text{O}, \text{As}_2\text{O}_5$ and $3\text{CuO}, 3\text{Na}_2\text{O}, 2\text{As}_2\text{O}_5$, were prepared.

The arsenic compounds described above and in preceding abstracts (*loc. cit.*) are slowly decomposed when strongly heated in a porcelain vessel. The alkali salts are stable at a dull red heat, but at about 1000° they lose oxygen and arsenious anhydride, the expulsion of the latter being probably the result of the action of silica, since the containing vessel is vigorously attacked. Calcium pyroarsenate is decomposed at a bright red heat, but the remaining simple salts usually undergo decomposition at a dull red heat; the double salts containing both alkali and metallic oxide are decomposed less readily than the simple salts of the corresponding metallic oxides.

Ammonium magnesium arsenate is decomposed at a comparatively low temperature in a vacuum, with liberation of water and ammonia, but, at a temperature approaching to a dull red heat, pure nitrogen is evolved and arsenious anhydride sublimes; the residue contains most of the arsenic acid combined with magnesium. When the double salt is heated strongly in a stream of oxygen, traces of arsenious anhydride are almost invariably liberated, so that the calcination of the salt may give rise to errors in quantitative work.

Sodium arsenate is slowly decomposed by hydrogen at an incipient red heat, with liberation of water and arsenic; at higher temperatures, the salt is quickly acted on, and finally sodium hydroxide, containing only traces of combined arsenic, is left. Most of the other arsenates are acted on in a similar manner, and usually more readily than the

sodium salt, but sometimes, as, for example, in the cases of cobalt arsenate and nickel potassium arsenate, the expulsion of the arsenic is very incomplete, owing to the formation of an arsenide. The arsenates are also reduced by carbonic oxide at a high temperature.

F. S. K.

Preparation of Carbon under High Pressure. By H. MOISSAN (*Compt. rend.*, 116, 218—224).—Experiments were made with the object of ascertaining the influence of pressure on the crystallisation of carbon at a high temperature. The various forms of carbon were isolated by successive treatment with hydrochloric or nitric acid, boiling sulphuric acid, hydrofluoric acid, and a mixture of nitric acid and potassium chlorate. Modifications of different sp. gr. were separated by means of bromal, or, more conveniently, methylene iodide, and bromoform, and mixtures of the two. The power to scratch rubies is shared by some metallic silicides, which also have a sp. gr. practically the same as that of the diamond, and hence the formation of carbonic anhydride by combustion in oxygen is necessary to characterise the latter.

When carbon is dissolved in iron between 1100° and 3000°, either graphite, or a mixture of graphite and amorphous carbon, separates on cooling under ordinary pressure, but, if the metal is allowed to cool under high pressure, the phenomena are different. A mass of iron is heated to from 2000° to 3000°, and the exterior is rapidly cooled by means of water; the still liquid interior expands as it gradually solidifies, and thus produces a very high pressure. Another method is to compress charcoal from sugar in a soft iron cylinder which is closed with a screw plug, and plunge the cylinder into a crucible containing melted wrought iron. The crucible is then withdrawn from the fire and placed in water until the exterior is cooled to a dull red heat, after which it is allowed to cool by exposure to air. Three forms of carbon are obtained, in proportions that depend on the conditions of cooling, namely, graphite, thin, contorted, maroon-coloured flakes, and diamond. The diamond is obtained as grains of grey-black *carbonado* of sp. gr. 3.0 to 3.5, and as transparent fragments with a cetaceous lustre, and parallel striæ or triangular markings. Both varieties, when burnt, leave minute quantities of ash, having all the characteristics of the ash of *carbonado* or diamond. The yield is, however, small, and the results are uncertain, neither diamond nor *carbonado* being obtained in many of the experiments.

Similar results can be obtained, although with even greater uncertainty, by dissolving carbon in iron melted at about 2000°, and rapidly cooling the metal in a current of coal gas.

Silver expands when solidifying, and also has the power of dissolving carbon. If a quantity of the metal is heated to boiling in a crucible brasqued with charcoal, and then rapidly cooled on the outside by immersing it in water, *carbonado* is obtained in small plates of sp. gr. from 2.5 to 3.5.

The silver used in these experiments contained a very small quantity of gold, and some of the grains of carbon were impregnated with this metal. Des Cloizeaux has observed that some specimens of natural *carbonado* enclose small globules of gold.

C. H. B.

Reproduction of Diamonds. By C. FRIEDEL (*Compt. rend.*, **116**, 224—226).—When carbon bisulphide is placed in a cavity cut in a block of mild steel and closed with a screw, and the whole is heated to dull redness or to bright redness, the bisulphide decomposes, leaving a residue of amorphous carbon, whilst the interior of the cavity is lined with a thin film of iron sulphide and the remainder of the sulphur is diffused throughout the steel to a distance of more than 15 mm. from the cavity.

If sulphur is heated in closed vessels at 500° with cast-iron turnings rich in carbon, and the product is treated with acids and finally with a mixture of nitric acid and potassium chlorate, a very small quantity of residue is left, in the form of a black powder which scratches corundum, but the quantity obtained was insufficient for analysis.

C. H. B.

Potassium-astrachanite, a new Potassium-magnesium Double Sulphate. By J. K. VAN DER HEIDE (*Ber.*, **26**, 414).—This substance, $\text{MgSO}_4, \text{K}_2\text{SO}_4 + 4\text{H}_2\text{O}$, is formed when a solution of schönite ($\text{MgSO}_4, \text{K}_2\text{SO}_4 + 6\text{H}_2\text{O}$) and sodium chloride is evaporated at 60° or from a solution of magnesium and potassium sulphates at 100°. It crystallises in tables, and is the potassium analogue of the already known sodium compound, astrachanite.

C. F. B.

Calcium Oxychloride. By B. ZAHORSKY (*Zeit. anorg. Chem.*, **3**, 34—43).—This substance is prepared by boiling lime with a concentrated solution of calcium chloride, or by dissolving excess of lime in hydrochloric acid, filtering, and allowing to cool. The salt crystallises in long, thin needles, which are lustrous, highly refractive, and transparent when fresh, but, if kept in the air, take up carbonic anhydride and become opaque. It dissolves in glycerol, but is decomposed by water, alcohol, and other solvents. It decomposes ammonium chloride with liberation of ammonia. Several analyses of the substance have already been made; those of the author agree well with the composition $3\text{CaO}, \text{CaCl}_2 + 15\text{H}_2\text{O}$. Probably the constitutional formula is $\text{HO} \cdot \text{Ca} \cdot \text{O} \cdot \text{Ca} \cdot \text{Cl} + 7\text{H}_2\text{O}$, for only 14 out of the 15 mols. of water are lost by drying in a vacuum.

The following table gives the grams of lime which dissolve at different temperatures in 100 c.c. of pure water, or of aqueous calcium chloride solutions of varying strength. In the cases marked *, a certain quantity of calcium chloride was precipitated from the solution as oxychloride.

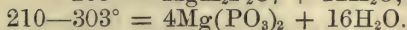
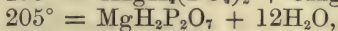
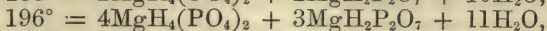
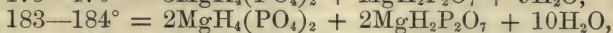
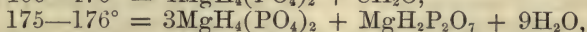
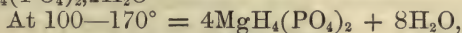
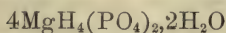
Temp.	Pure water.	CaCl_2 , 5 p. c.	CaCl_2 , 10 p. c.	CaCl_2 , 15 p. c.	CaCl_2 , 20 p. c.	CaCl_2 , 25 p. c.	CaCl_2 , 30 p. c.
20°	0·1374	0·1370	0·1661	0·1993	0·1857*	0·1661*	0·1630*
40	0·1162	0·1160	0·1419	0·1781	0·2249	0·3020*	0·3684*
60	0·1026	0·1020	0·1313	0·1706	0·2204	0·2989	0·3664
80	0·0845	0·0936	0·1328	0·1736	0·2295	0·3261	0·4122
100	0·0664	0·0906	0·1389	0·1842	0·2325	0·3710	0·4922

C. F. B.

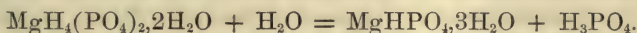
Constitution of Bleaching Power. By G. LUNGE (*Zeit. anorg. Chem.*, **2**, 311—313).—The author calls attention to the fact that the reactions of bleaching powder, recently observed by Mijers (this vol., ii, 209), form an independent confirmation of the results previously published by him, and are likewise best explained by assuming that the compound has the formula attributed to it by Odling.

G. T. M.

Monomagnesium Phosphate. By J. STOKLASA (*Zeit. anorg. Chem.*, **3**, 67—75; compare this vol., ii, 168).—This salt, $\text{MgH}_4(\text{PO}_4)_2 + 2\text{H}_2\text{O}$, is decomposed at different temperatures in the manner represented by the following equations.



It is not decomposed by water, even at 60° . Absolute and aqueous alcohol both decompose it completely at 100° , if in large excess, according to the equation



The dimagnesium phosphate thus obtained has been hitherto unknown; it forms crystals with a nacreous lustre, and dissolves sparingly in water, readily in acids.

C. F. B.

Preparation of Sulphites of Zinc, Manganese, and Cadmium.

By G. DENIGÈS (*Bull. Soc. Chim.* [3], **7**, 569—573).—Zinc sulphite, $\text{ZnSO}_3 + 2\frac{1}{2}\text{H}_2\text{O}$, is prepared by mixing in the cold 25 per cent. solutions of zinc sulphate and sodium sulphite, the first acidified with acetic acid, when it separates, after 12—15 hours, in clinorhombic prisms.

Manganese sulphite, $\text{MnSO}_3 + 3\text{H}_2\text{O}$, obtained by mixing 10 per cent. solutions of manganese sulphate acidified with acetic acid and sodium sulphite, crystallises in oblique prisms; whilst a monohydrate, which is formed when the additive compound $\text{MnSO}_3, 2\text{NH}_2\text{Ph}, \text{H}_2\text{SO}_3$ is dissolved in boiling water, crystallises in rhombic prisms.

Cadmium sulphite, $\text{CdSO}_3 + 3\text{H}_2\text{O}$.—This salt separates on mixing equal volumes of 10 per cent. solutions of cadmium sulphate acidified with acetic acid and sodium sulphite. The author failed to obtain Muspratt's dihydrate (*Phil. Mag.* [3], **30**, 414).

A. R. L.

Stas's Determinations of the Atomic Weight of Lead. By G. HINRICHS (*Compt. rend.*, **116**, 431—433).—According to the author, the determinations of the atomic weight of lead by Stas contain the same systematic error that exists in the determinations of the oxygen in potassium chlorate (this vol., ii, 163). The values obtained for the atomic weight are functions of the amounts of lead used in the deter-

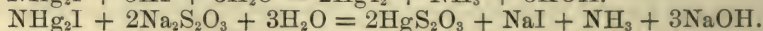
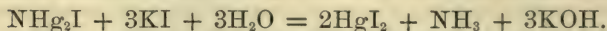
minations. The proof for this case is not, however, so convincing a one as that for the chlorate. H. C.

Mixed Double Haloids of Lead and Potassium. By C. H. HERTY (*Amer. Chem. J.*, **15**, 81—104; compare Abstr., 1892, 779).—The crystals obtained by cooling hot solutions of lead bromide in potassium iodide, and by crystallising cold solutions of the same, all proved to be the salt $\text{KPbI}_3 + 2\text{H}_2\text{O}$. By dissolving lead iodide in an aqueous solution of potassium bromide, two classes of crystals were generally obtained: needle-shaped crystals, which proved to be isomorphous mixtures of $\text{KPbI}_3 + \text{H}_2\text{O}$ and $\text{KPbBr}_3 + \text{H}_2\text{O}$, and tabular crystals which were mixtures of varying proportions of potassium lead iodide, KPbI_3 , potassium lead bromide, KPbBr_3 , and lead bromide. The existence of such mixed double haloids as KPbI_2Br and KPbIBr_2 has, therefore, not yet been proved. (Compare Richardson's conclusion, Abstr., 1892, 784.) A. G. B.

Thallium Sulphite. By K. SEUBERT and M. ELTEN (*Zeit. anorg. Chem.*, **2**, 434—436).—On mixing solutions of thallium sulphate and sodium sulphite, *thallium sulphite* is precipitated as a white, granular, crystalline powder. It is insoluble in alcohol, but dissolves readily in warm water, and the solution, on being slowly cooled, deposits the salt in the form of feathery aggregates of slender needles. At 15.5° , 100 parts of water dissolve 3.34 parts of the salt. Its sp. gr. at 19.8° is 6.4273. G. T. M.

Graphochemical Calculation. By E. NICKEL (*Zeit. physikal. Chem.*, **11**, 265—274).—The principles described and employed in previous papers (Abstr., 1892, 1158; this vol., ii, 115 and 119) are applied to the discussion of the different processes involved in the reduction of copper from its ores. H. C.

Action of Potassium Iodide or Sodium Thiosulphate on Mercurammonium Salts. By E. BALESTRA (*Gazzetta*, **22**, ii, 557—563).—Mercurammonium salts are dissolved by potassium iodide or sodium thiosulphate solutions with liberation of ammonia and alkali, in accordance with the following equations:—



The author has performed these reactions for a number of mercurammonium salts, and determined the ammonia by distillation and the remaining alkali by direct titration; the results obtained agree well with the theoretical values. Similar reactions occur in the case of double salts such as $\text{NH}_4\text{HgCl}_2, \text{NH}_4\text{Cl}$. W. J. P.

Decomposition of Alkali Aluminates in presence of Alumina. By A. DITTE (*Compt. rend.*, **116**, 183—185).—When crystallised potassium aluminate is dissolved in water, it partially decomposes with separation of alumina. If the solution is filtered after a few minutes, it is limpid, but if kept in a closed vessel, it gradually de-

composes with separation of alumina, which attaches itself to the sides of the vessel in the form of a strongly adherent crust of small, transparent crystals of the same composition as gibbsite, $\text{Al}_2(\text{OH})_6$.

The same decomposition can be observed if a solution of any aluminium salt is mixed with potassium hydroxide in quantity not quite sufficient to redissolve the precipitated aluminium hydroxide.

A solution containing a very slight excess of potassium hydroxide above that required to dissolve the aluminium hydroxide will remain clear for many months.

When the quantity of alkali is not quite sufficient to keep the whole of the alumina in solution, a condition of equilibrium is established between the aluminate, the alumina, the alkali hydroxide, and the water. Any local variation of temperature disturbs this equilibrium, and a small quantity of alumina separates and crystallises in the form of gibbsite. This crystallised form is less soluble than the gelatinous form, and does not redissolve even when the temperature reverts to its original value. Consequently there is a further disturbance of the equilibrium, more alumina separates, and in contact with the gibbsite already formed, crystallises and becomes less soluble, and this change goes on until equilibrium is established between the aluminate, the alkali hydroxide, water, and gibbsite.

The accuracy of this view is proved by the fact that anything that promotes contact of the solution with the separated alumina accelerates the change and *vice versâ*. The phenomena and the explanation of them are the same in the case of sodium hydroxide.

C. H. B.

Decomposition of Alkali Aluminates by Carbonic Anhydride.

By A. DITTE (*Compt. rend.*, 116, 386—388).—When potassium carbonate solution is added drop by drop to a solution of potassium aluminate, a precipitate forms and at first redissolves, but afterwards becomes permanent; it has the composition $3\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 5\text{CO}_2$. Potassium hydroxide is formed at the same time, and since it is capable of decomposing the double carbonate, a condition of equilibrium is established.

When carbonic anhydride is allowed to fall on the surface of a solution of potassium aluminate containing a small excess of alkali, potassium carbonate is formed, but no precipitation of the double carbonate takes place until the greater part of the excess of alkali has been neutralised. At this point, the water decomposes a small quantity of the aluminate, and the liberated alumina dissolves at first in the potassium hydroxide, but quickly separates in crystals of the hydroxide, $\text{Al}_2(\text{OH})_6$; there can no longer be equilibrium, and the aluminate decomposes more or less rapidly.

If carbonic anhydride is passed into a similar solution until a permanent precipitate of the double carbonate and the crystallised hydroxide begins to form, and the flask is then closed, a heavy precipitate of the double carbonate at first settles, but is gradually decomposed by the potassium hydroxide liberated by the decomposition of the aluminate by water, and crystallised aluminium hydroxide separates.

If the solution of the aluminate contains a considerable excess of alkali, and carbonic anhydride is passed into it until a permanent precipitate begins to form, and the flask is then closed, a precipitate

of the double carbonate separates, but as there is still sufficient potassium hydroxide in the liquid to prevent decomposition of the aluminate, crystallised aluminium hydroxide is not formed. A similar result is obtained if potassium carbonate is first added to the solution until the precipitate redissolves with difficulty, and carbonic anhydride is then passed into the liquid until a permanent precipitate is formed. In both cases, if the passage of the carbonic anhydride is continued too long, too much of the alkali is neutralised and the aluminate gradually decomposes.

C. H. B.

Action of Hydrogen Ammonium Sulphate on Glass. By M. LACHAUD and C. LEPIERRE (*Bull. Soc. Chim.* [3], 7, 603—608).—Weighed pieces of glass rod, 20 mm. in length, were heated for 60 hours with an excess of fused hydrogen ammonium sulphate, the salt being renewed as it volatilised, the glass finally washed with hot water, and the loss in weight determined. A sample of ordinary soda-lime glass lost as much as 21.5 per cent. of its weight; it had then the appearance of porcelain, and could be reduced to powder under the pressure of the hand. By analyses of the sample before and after this treatment, the loss was found to be mainly due to sodium oxide; it amounted to 20 per cent. of sodium oxide out of 22 per cent. originally present. When heated with concentrated sulphuric acid for 40 hours, the same glass lost only 0.05 per cent. On fusion with hydrogen ammonium sulphate, Bohemian glass lost 12 per cent., and crystal glass 10 per cent., of their weight, 10 and 8 per cent. respectively of which represented potassium oxide. The authors find that by fusing together a mixture of potassium sulphate and ammonium hydrogen sulphate, 9 per cent. of the potassium sulphate is volatilised with the ammonium salt.

A. R. L.

Action of Water Vapour on Ferric Chloride. By G. ROUSSEAU (*Compt. rend.*, 116, 188—190).—When anhydrous ferric chloride is heated in a glass tube in a slow current of carbonic anhydride saturated with aqueous vapour, brownish-red needles of the oxychloride $\text{Fe}_2\text{Cl}_6 \cdot 2\text{Fe}_2\text{O}_3$ are formed between 275° and 300° , and darker and larger needles of the oxychloride $\text{Fe}_2\text{Cl}_6 \cdot 3\text{Fe}_2\text{O}_3$. It follows that the decomposition of ferric chloride in presence of water vapour is strictly analogous to its decomposition in concentrated solutions (*Abstr.*, 1892, 119—120). Between a dull red heat and the softening point of glass, no sublimate is formed when the ferric chloride is in excess, but hexagonal lamellæ of hematite are obtained when the water vapour is in excess. The non-formation of an oxychloride or the oxide at a dull red heat when the chloride is in excess is probably due to the occurrence of some reverse reaction.

C. H. B.

Mixed Crystals of Ammonium and Ferric Chlorides. By J. L. C. SCHROEDER VAN DER KOLK (*Zeit. physikal. Chem.*, 11, 167—173).—The observations of Roozeboom (*Abstr.*, 1892, 1384) on mixed crystals of ammonium and ferric chlorides have been extended by the author, and mixed crystals of ammonium chloride with the chlorides of cobalt, nickel, and cadmium also examined. A detailed description

of the appearance of some of the crystals is given. The author considers it probable that the ferric chloride crystals are isomorphous mixtures of ammonium chloride with a regular modification of ferric chloride, perhaps $\text{Fe}_2\text{Cl}_6 \cdot 8\text{H}_2\text{O}$. In the other cases, isomorphous mixtures are probably not formed. H. C.

Preparation of Chromium and Manganese at a High Temperature. By H. MOISSAN (*Compt. rend.*, 116, 349—351).—When manganous oxide is mixed with charcoal and heated in the arc formed by a current of 60 volts and 300 ampères, reduction is complete in 5 or 6 minutes; with 50 volts and 100 ampères, reduction requires 12 to 15 minutes. In presence of excess of carbon, the reduced metal contains 6·4 to 14·6 per cent. of that element, but in presence of excess of manganous oxide, the reduced metal contains only 4 to 5 per cent. of carbon. When the proportion of carbon is low, the metal remains unaltered even in open vessels, but with a higher proportion of carbon, it is attacked by atmospheric moisture. Small fragments placed in water are completely attacked in 24 hours, hydrogen and hydrocarbons being given off.

Chromium oxide mixed with carbon is reduced in from 8 to 10 minutes with a current of 50 volts and 350 ampères, about 100 grams of the metal being obtained. With 50 volts and 100 ampères, reduction requires about 15 minutes. The proportion of carbon in the reduced metal varies from 8·6 to 12·85 per cent., but if this product is broken up, placed in a carbon crucible brasqued with chromic oxide, covered with the same oxide and again subjected to the action of the arc, metallic chromium is obtained quite free from carbon.

Chrome iron ore can be reduced in the same manner, a homogeneous alloy of chromium and iron being obtained. C. H. B.

Crystalline Forms of Chromium and Iridium. By W. PRINZ (*Compt. rend.*, 116, 392—395).—Chromium prepared by Woehler's method forms minute cubes with pyramidal faces, the symbol being, approximately, $b\frac{5}{3}$, this form giving rise to the hexagonal and octagonal contours seen when the powder is examined by transmitted light. The rhombohedra described by previous observers are very probably deformed octahedra.

Iridium prepared by Stas in the form of a highly lustrous powder was seen under the microscope to consist of regular hexagonal lamellæ, triangles, small crosses, and regular octahedra. All the other forms are derived from the regular octahedron, the triangles being flattened tetrahedra, whilst the hexagons arise from the deformation of the octahedron along one of its faces. All the forms closely resemble the crystallites of copper observed in aventurine. It follows that, so far as Stas's preparation shows, iridium is not dimorphous and does not crystallise in the hexagonal (rhombohedral) system.

C. H. B.

Chromium Fluorides. By C. POULENC (*Compt. rend.*, 116, 253—256).—*Chromous fluoride*, CrF_2 , is obtained by the action of gaseous hydrogen fluoride on metallic chromium at a red heat, or by the action of the same gas on chromous chloride at the ordinary tempe-

perature. After fusion it forms a transparent green mass, with a nacreous lustre, and a very brilliant, lamellar, crystalline fracture; sp. gr. 4.11. It is insoluble in alcohol, and only slightly soluble in water, dissolves in boiling hydrochloric acid, is very slightly attacked by nitric acid, and is but slowly attacked even by boiling sulphuric acid. It is reduced by hydrogen at a dull red heat, and when heated in the air is converted into chromic oxide. At a red heat, it is decomposed by hydrogen chloride, by water vapour with formation of hydrogen fluoride and chromic oxide, and by hydrogen sulphide with formation of black chromium sulphide and hydrogen fluoride. Fused potassium nitrate attacks chromous fluoride readily with formation of normal potassium chromate; fused alkali carbonates first convert it into an alkali fluoride and chromium oxide, whilst at a higher temperature a normal chromate is formed.

Chromic fluoride, Cr_2F_6 , is obtained in a crystalline form by the action of gaseous hydrogen fluoride on anhydrous chromic chloride, precipitated chromic oxide, hydrated chromic fluoride, or amorphous anhydrous chromic fluoride.

When chromic chloride is heated to dull redness in hydrogen fluoride, anhydrous chromic fluoride is formed, and if the tube is heated at 1200° , part of the product volatilises, and condenses in very slender needles, whilst the non-volatilised portion solidifies to a deep green mass, on the surface of which are long, well-defined, highly refractive, green prisms. All three forms have the same composition.

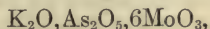
C. H. B.

Complex Inorganic Acids. By F. KEHRMANN (*Zeit. anorg. Chem.*, **3**, 76—77).—Under certain circumstances, to be described later, reddish-yellow phosphomolybdates have been obtained; the potassium and ammonium salts dissolve readily in water. The corresponding acid has been obtained in the free state.

C. F. B.

Molybdoarsenates. By C. FRIEDHEIM (*Zeit. anorg. Chem.*, **2**, 314—410; compare *Abstr.*, 1890, 1066; 1891, 884).—A number of molybdoarsenic acids were prepared by Pufahl, by the addition of sulphuric acid to a mixture of barium molybdate and arsenic acid, and salts of the same acid were obtained by boiling together solutions of the alkali arsenates and molybdic acid. On heating a solution of potassium arsenate, KH_2AsO_4 , with molybdic anhydride, several products are formed. The first has the composition $\text{K}_2\text{O}, \text{As}_2\text{O}_5, 6\text{MoO}_3 + 5\text{H}_2\text{O}$, and is identical with one of the compounds obtained by Pufahl in the above-mentioned way. It forms characteristic, microscopic, octahedral crystals. The second product forms rhombohedral crystals, having the composition $3\text{K}_2\text{O}, \text{As}_2\text{O}_5, 18\text{MoO}_3 + 26\text{H}_2\text{O}$, and is identical with the compound obtained by the addition of potassium carbonate to an aqueous solution of the red-coloured molybdoarsenic acid $\text{As}_2\text{O}_5, 18\text{MoO}_3 + 28\text{H}_2\text{O}$, which is the third well-characterised product of the action. In a similar way, this acid and the salt $3\text{Na}_2\text{O}, \text{As}_2\text{O}_5, 18\text{MoO}_3 + 24\text{H}_2\text{O}$ were obtained from monosodium arsenate. The nature of the pro-

ducts in all these cases depends not only on the quantity of molybdc anhydride employed, but also on the nature of the alkali arsenate. When dipotassium arsenate and molybdc anhydride are allowed to interact in molecular proportion, the compound $3\text{K}_2\text{O}, \text{As}_2\text{O}_5, 6\text{MoO}_3 + 25\text{H}_2\text{O}$ is obtained, and the sodium salt, $3\text{Na}_2\text{O}, \text{As}_2\text{O}_5, 6\text{MoO}_3 + 11\text{H}_2\text{O}$, is formed in a similar way. On employing a large excess of molybdc acid, the compound $3\text{K}_2\text{O}, \text{As}_2\text{O}_5, 24\text{MoO}_3 + 12\text{H}_2\text{O}$, previously prepared by Pufahl, is obtained. In short, all the compounds previously prepared, in addition to several new ones, are to be obtained directly from their components. The author discusses, at length, the considerations which have led him to ascribe the formula $\text{AsO}(\text{OH})_2 \cdot \text{O} \cdot \text{MoO}_2 \cdot \text{O} \cdot \text{MoO}_2 \cdot \text{O} \cdot \text{MoO}_2 \cdot \text{OK}$ to the compound



and the constitution $\text{AsO}(\text{O} \cdot \text{MoO}_2 \cdot \text{O} \cdot \text{MoO}_2 \cdot \text{O} \cdot \text{MoO}_2 \cdot \text{OK})_3$ to the compound $3\text{K}_2\text{O}, \text{As}_2\text{O}_5, 18\text{MoO}_3$. By substituting the groups $\text{Mo}(\text{OH})_4$ for MoO_2 in these formulæ, it is possible also to account for the water molecules existing in the compounds. G. T. M.

Preparation of Uranium at a High Temperature. By H. MOISSAN (*Compt. rend.*, 116, 347—349).—The mixture of oxides obtained by strongly heating uranium nitrate is mixed with a slight excess of carbon, and strongly compressed into a carbon crucible, which is then embedded in magnesia, and subjected in an electrical furnace to the arc formed by a current of 60 volts and 450 ampères. Reduction takes almost immediately, and an ingot of 200 to 220 grams is obtained in 12 minutes. The metal is very hard, and has a brilliant fracture; it is not pure, but contains from 5 to 13·5 per cent. of carbon. Its melting point is higher than that of platinum, but it decomposes water at the ordinary temperature. C. H. B.

The Determination of Equivalents by Conversion of Oxides into Sulphates. The Separation of the Gadolinite Metals. By G. KRÜSS (*Zeit. anorg. Chem.*, 3, 44—59).—Attention is called to the fact that the presence of impurities, even when as much as 1 per cent., cannot always be detected by the spectroscope, and in the case of compounds of the rare earths, the use of quantitative analysis is recommended, in order to ascertain if two successive fractions are identical or different. Of the various methods, the author prefers the conversion of an oxide into a sulphate by treating it in a crucible with dilute sulphuric acid, evaporating, and then igniting gently, at about 350°. The method is trustworthy, and no basic sulphate is formed; Bailey's statement (*Trans.*, 1887, 676) that no constant weight can be obtained is shown by experiment to be incorrect. The use of a porcelain crucible is admissible.

At the end of the paper is given a synopsis of the methods at present in use for separating metals of the cerium and ytterbium groups. It is too long to reproduce here; but the following are the heads under which the methods are arranged:—I. Crystallisation of double salts. II. Precipitation of basic salts. III. Fractional pre-

cipitation of the earths in various forms. IV. Fractional solution. V. Oxidation (only in case of cerium). C. F. B.

Electrolysis of Solutions of Metals of the Rare Earths. By G. KRÜSS (*Zeit. anorg. Chem.*, **3**, 60—62).—If a solution containing chlorides of the rare earth metals is electrolysed, hydrogen and chlorine are evolved at the two poles, and the oxides of the metals are precipitated. It is obvious that the last metal to separate out will be that one which has the greatest tendency to combine with chlorine, and it should be possible to effect at least a partial separation of the metals by fractional electrolysis. An experiment actually showed that, when a mixture was precipitated in three fractions with aniline, and the middle fraction again separated into five by fractional electrolysis, the electrolysis effected a separation in the same sense as the precipitation. The vessel used was a beaker of 15 cm. diameter; inside it, and touching the glass, was a cylinder of copper gauze reaching to the top of the liquid, and forming the negative electrode; the positive electrode was a rod of gas carbon placed in the axis of the beaker. The battery contained four Bunsen elements joined in series. C. F. B.

Double Halogen Compounds of Gold. By G. KRÜSS and F. W. SCHMIDT (*J. pr. Chem.* [2], **47**, 301—302).—The authors cannot admit that AuBr_2 or Au_2Br_4 is produced by the action of bromine on gold under the conditions of Thomsen's experiments (*Abstr.*, 1888, 559). They are not convinced by Petersen's arguments (*this vol.*, ii, 126), and still maintain that AuBr_3 is the ultimate product of the action of bromine on gold. A. G. B.

Rapid Reduction of Potassium Platinochloride. By H. BORNTRÄGER (*Zeit. anal. Chem.*, **32**, 188).—The precipitate is dissolved in hot water and potassium oleate added. This produces a precipitate containing 58 per cent. of oleic acid, 23 per cent. of platinum, and 19 per cent. of potassium chloride. Ignited for a few minutes, it decomposes very readily, leaving a mixture of very active platinum black with potassium chloride; the latter can be removed by washing with hot water. M. J. S.

Atomic Weight of Palladium. By A. JOLY and E. LEIDIE (*Compt. rend.*, **116**, 146—148).—Pure palladium was converted into potassium palladionitrite, and the latter into potassium palladiochloride, which was carefully recrystallised, and dried at 100° . It was then electrolysed in aqueous solution acidified with hydrochloric acid, the deposited metal being heated in a current of hydrogen, and allowed to cool in a current of carbonic anhydride; as a mean of eight determinations, $\text{Pd} = 105.438$, when $\text{H} = 1$, $\text{O} = 15.96$, and $\text{Cl} = 35.37$. This value is almost identical with that obtained by Bailey and Lamb, 105.459 (*Trans.*, 1892, 745—753).

Reduction of the palladiochloride in hydrogen gave, as a mean result of two experiments, $\text{Pd} = 105.665$, but the experiments are being continued. C. H. B.

Physical Properties of Fused Ruthenium. By A. JOLY (*Compt. rend.*, 116, 430—431).—Ruthenium can be fused and obtained in ingots of 25 to 30 grams by means of the electric arc. In order to avoid volatilisation as far as possible, the metal should be heated very rapidly. The metal, after treatment with aqua regia and hydrofluoric acid, is heated in hydrogen to reduce the superficial film of oxide. It then has a grey colour, more like that of iron than of platinum, its hardness is comparable to that of iridium, and it is brittle when cold, but somewhat malleable at a red heat. The sp. gr. of the fused and powdered metal at 0°, compared with water at 4°, is 12·063.

C. H. B.

Mineralogical Chemistry.

Origin of the Diamond. By J. WERTH (*Compt. rend.*, 116, 323—326).—Consideration of the mode of occurrence, crystalline form and aspect, and the general physical and chemical properties of the diamond leads the author to conclude that diamonds have been formed under pressure at a high temperature in presence of hydrogen containing more or less carbon, and have been cooled rapidly. Bort contains 0·5 per cent. of hydrogen, and when heated under water, gives off bubbles of gas.

C. H. B.

Graphite, Carbonado, and Microscopic Diamonds in Blue Earth from the Cape. By H. MOISSAN (*Compt. rend.*, 116, 292—295).—Blue earth from De Beer's Mine was treated with boiling sulphuric acid for several hours, washed, treated with aqua regia, and again washed. It was then subjected to repeated alternate treatment with hydrofluoric and sulphuric acids. 2 kilos. of the earth left only a very minute quantity of a residue containing brilliant, hexagonal or lamellar crystals of graphite which yielded a greenish graphitic oxide when treated in the usual way, together with microscopic grains of carbonado and diamonds, mixed with amber-yellow grains and long, transparent, non-combustible prisms, both of which can be decomposed by fusion with potassium hydrogen sulphate and subsequent treatment with hydrofluoric and sulphuric acids. Carbonado has previously been detected in the blue earth by Couttolenc, who, however, did not recognise the presence of microscopic diamonds.

C. H. B.

Cupro-iodargyrite, a new Mineral. By H. SCHULZE (*Chem. Zeit.*, 16, 1952).—Among some minerals from the San Agustin Mine, Iquique, Chili, the author found specimens of a copper silver iodide, hitherto not observed in nature. The new mineral has a sulphur-yellow colour with an adamantine lustre. On analysis, it yielded the following results:—

C.	Ag.	I.
15·91	25·58	57·75

These results are in accord with those demanded by the formula CuI,AgI (compare Abstr., 1891, 1436). B. H. B.

Cuproplumbite from Butte City, Montana. By J. T. DE BELL (*Amer. Chem. J.*, **14**, 620—621).—An analysis of this substance gave—

Cu.	Pb.	S.	SiO_2 .	Total.
61.32	18.97	17.77	1.58	99.64

This agrees approximately with the formula $5\text{Cu}_2\text{S,PbS}$. The mineral is amorphous, of bluish-grey-black colour, lustre submetallic, fracture uneven, fuses with spitting, sp. gr. = 5.39, hardness = 2.5. From considerations regarding its specific gravity, it is classed rather with galena than with chalcosite. C. F. B.

Platiniferous Nickel Ore from Canada. By F. W. CLARKE and C. CATLETT (*Chem. News*, **67**, 53—54; from *Bull. U.S. Geol. Surv.*, No. 64).—An analysis of nickel ore from the mines at Sudbury, Ontario, gave the following results:—

Ni.	Fe.	SiO_2 .	Cu.	S.	Total.
41.96	15.57	1.02	0.62	40.80	99.97

These figures correspond approximately with the formula Ni_3FeS_5 . In short, the mineral has the composition Ni_4S_5 , with about one-fourth of the nickel replaced by iron. The only known species with which this agrees is Laspeyres's polydymite, of which the Sudbury mineral is evidently a ferriferous variety. The peculiarity of this ore is that it contains platinum in appreciable quantities, three specimens of the Sudbury ore assayed showing respectively 0.0087, 0.006, and 0.024 per cent. of platinum. Probably the platinum exists in the ore as sperrylite. B. H. B.

Brazilite. By E. HUSSAK (*Jahrb. f. Min.*, 1893, i, Mem. 89).—An analysis of the monoclinic mineral brazilite by C. W. Blomstrand showed that it consists of pure zirconia, the analytical results being as follows:—

ZrO_2 .	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO.	MgO.	Alkalis.	Loss.	Total.
96.52	0.70	0.43	0.41	0.55	0.10	0.42	0.39	99.52

B. H. B.

Statuary Marble from Rutland, Vermont. By J. T. DE BELL (*Amer. Chem. J.*, **14**, 626—627).—This marble is very pure, containing as impurities only the following percentage amounts:— SiO_2 , 0.167; Fe_2O_3 and Al_2O_3 , 0.062; Na_2O , 0.065; K_2O , 0.004; MgO , 0.079. The lime prepared from it is but little inferior to that from Carrara marble, if required for the separation, in analysis, of magnesia from alkalis. C. F. B.

Electrical Calamine from Wythe Co., Virginia. By A. JONES (*Amer. Chem. J.*, **14**, 621).—A peculiarly pure specimen of

$\text{ZnSiO}_4 + \text{H}_2\text{O}$. It occurs occasionally as a layer of bright, transparent, colourless crystals, encrusting to a depth of 1—2 mm. the snow-white opaque sheets of the ordinary ore. C. F. B.

The Mesotype Group in the Puy-de-Dôme. By F. GONNARD (*Jahrb. f. Min.*, 1893, i, Ref. 247; from *Bull. soc. fran. min.*, 14, 165—174).—The zeolite described by Guilleruin as mesotype from the Puy-de-Dôme is shown by analysis to be scolezite. It was, however, probably not derived from the Puy-de-Dôme, for all the mesotypes of this district examined by the author are shown to be natrolite. The following are the results of two analyses, I, mesotype from the Puy-de-Marman, and II, from the Tour de Gevillat:—

	SiO_2 .	Al_2O_3 .	Na_2O .	CaO .	H_2O .	Total.
I.	48·03	26·68	15·61	—	9·62	99·94
II.	47·88	26·12	15·63	0·45	9·80	99·88

B. H. B.

Paranthrite from Clay Co., N. Carolina. By W. N. BERKELEY (*Amer. Chem. J.*, 84, 628).—This mineral occurred in a corundum mine, in a pocket near the centre of a 6-foot vein, consisting of decomposed albite, corundophilite, and chloritic minerals, lying between chrysolite and horblende gneiss. It consists of bluish-grey, rounded, crystalline lumps; sp. gr. = 2·75, hardness = 5·5, composition:—

SiO_2 .	Al_2O_3 .	CaO .	Na_2O .	H_2O .
47·54	34·03	17·23	1·82	1·02

C. F. B.

Glaucanite from Hanover Co., Virginia. By M. B. CORSE and C. BASKERVILLE (*Amer. Chem. J.*, 14, 627—628).—This occurs in a bed of greensand marl. It appears as rounded grains interspersed with seams of quartz and with some spots of a much deeper green colour than the main portion. It is almost insoluble in strong acids, but after gentle ignition, when it turns brown, it is completely gelatinised by hydrochloric acid. II has a sp. gr. = 2·83, fusibility = 4·5.

	SiO_2 comb.	Quartz.	Al_2O_3 .	Fe_2O_3 .	FeO .	MgO .	CaO .	K_2O .
I.	43·34	8·22	6·62	15·16	8·33	0·95	0·62	4·15
II.	47·43	2·76	7·33	12·03	9·43	2·90	0·57	5·75
			Na_2O .	H_2O .	Total.			
			I. 1·84	10·32	99·55			
			II. 0·42	9·85	98·49			

C. F. B.

Constitution of Spherulites in Acid Eruptive Rocks. By W. CROSS (*Jahrb. f. Min.*, 1893, i, Ref. 294—297; from *Bull. Phil. Soc. Washington*, 11, 411—444).—The author regards microfelsite as a mechanical mixture of quartz and felspar (chiefly orthoclase) in varying quantities. Among the spherulites in the rocks of Rosita Hills and Silver Cliff, he has not found one that is not composed of definite minerals. Analysis of two obsidians, from Silver Cliff, with large

spherulites, and from Rosita Hills, shows that the glass consists almost exclusively of alkalis and alumina (in the felspar ratio), silicic acid, and water.

B. H. B.

The Meteorite from Cañon Diablo. By H. MOISSAN (*Compt. rend.*, 116, 288—290, and C. FRIEDEL, *ibid.*, 290—991).—Part of the meteorite from Cañon Diablo (Abstr., 1892, 284, 497; this vol., ii, 174), when treated with hydrochloric acid until all the iron was dissolved, left a residue of carbon in the form of an impalpable powder, thin maroon-coloured plates, similar to those obtained from iron cooled under pressure, and rounded fragments of high density. The latter, when treated with nitric acid and potassium chlorate, left two yellowish fragments, with a fatty lustre and a general appearance recalling the contorted crystallisation of bort. They scratched ruby easily, and one of them when burnt in oxygen yielded carbonic anhydride. The larger of the two fragments measured 0·7 by 0·3 mm. The denser carbon was associated with a grey substance in dendritic masses, which somewhat resembled platinum, but was not attacked by aqua regia. The meteorite is very far from being uniform in composition, considerable differences being observed in parts not more than 10 mm. distant from one another.

Friedel has not found in the same meteorite such large fragments of diamond, but has recognised amongst the microscopic grains of carbonado that he obtained, a certain number of small, transparent grains, which are, doubtless, white diamond. The dendritic substance is an iron sulphide, the composition of which corresponds with the formula Fe_8S .

C. H. B.

Physiological Chemistry.

Elimination of Carbonic Oxide. By L. DE SAINT-MARTIN (*Compt. rend.*, 116, 260—263).—When a rabbit partially poisoned by carbonic oxide, is placed under such conditions that natural elimination is impossible, as in a Regnault and Reiset's apparatus filled with air containing a known quantity of carbonic oxide, a certain quantity of the gas is slowly but regularly destroyed, the destruction taking place more actively the smaller the quantity of carbonic oxide that the animal has inhaled.

In estimating the proportion of carbonic oxide necessary to make a confined atmosphere fatally poisonous, the time during which the gas is inspired is an important factor, and it is probable that the quantity required is much smaller than has hitherto been supposed, provided that respiration of the mixture is continued for several hours.

C. H. B.

The Influence of certain Sulphur Compounds on Metabolism. By W. J. SMITH (*Zeit. physiol. Chem.*, 17, 459—467).—In a previous communication (*Therap. Monatsh.*, November, 1888), it

was shown that by metabolic changes sulphonal is converted into ethylsulphonic acid, whilst sulphuric acid is not formed in appreciable quantities. The present research relates to other sulphur compounds, and the experiments were carried out on a dog. For three days the animal received 1 lb. of dog biscuit and 1 litre of water daily. This was followed by a period of three days in which the drug was given in addition. The urine in the two periods was collected, analysed, and compared.

Acetone Ethylmercaptol.—There is no increase in the total sulphuric acid excreted, but qualitative examination showed the presence of an organic sulphur compound, which is readily soluble in water. Considering the near relationship of the drug given to sulphonal, it is probable that this compound is ethylsulphonic acid. The urine also contains small quantities of sulphonal.

α -Trithioaldehyde, $C_6H_{12}S_3$.—This is well absorbed from the intestine. The urine contains a small quantity of a sulphonate containing 39.3 per cent. of sulphur. Analysis of its crystals (m. p. 230°) agrees with the formula $C_6H_{12}S_3O_4$. The greater part of the sulphur appears in the urine as sulphuric acid.

Thioglycollic acid.—This causes sickness, but a small amount is absorbed, and leads to an increase in the urinary sulphates.

Ethylidenediethylsulphone.—There is a very slight rise in the urinary sulphates, and a small quantity of the drug was recovered unchanged from the urine.

Ethylenediethylsulphone.—There was no rise in the urinary sulphates.

The general conclusion drawn is, that urinary sulphates do not normally originate by oxidation of the sulphur-containing radicles in proteid matter, but by oxidation of sulphur compounds analogous to thioglycollic acid, cystin, and cystein.

W. D. H.

Phosphorus and the Lecithins. By W. MAXWELL (*Amer. Chem. J.*, 15, 185—195).—It has been shown in previous papers (Abstr., 1891, 489 and 511) that during the germination of seeds, the ratio of inorganic to organic phosphorus, presumably in the forms of phosphates and lecithins respectively, gradually decreases, the increase of the organic corresponding with the decrease of the inorganic phosphorus. It is now shown that during the development of the hen's egg, the ratio of inorganic to organic phosphorus gradually increases, the organic phosphorus, presumably in the form of lecithins, being converted into the phosphates of the bone of the chick. The lecithins were extracted from the yolk by alcohol and ether in succession, and the phosphorus of the extract converted into phosphate and weighed as magnesium pyrophosphate. The amount of phosphorus present in the form of nucleins, and in the shell, is so minute as to be negligible. At a certain stage in the development, the organic phosphorus was observed to increase for a time, a phenomenon which may be attributed to the conversion of the original inorganic phosphates of the egg into lecithins by the organism, previously to reconversion into bone phosphates.

JN. W.

Alkaloids in Cod Liver Oil. By J. BOUILLOT (*Compt. rend.*, 116, 439—441).—The alkaloids of cod liver oil are of biliary origin, and pre-exist in normal hepatic tissue; they are not produced by any process of fermentation. If a thin section of the fresh tissue is exposed to gaseous hydrogen fluoride or hydrogen chloride for half an hour, and then dried under a bell-jar, numerous crystals can be observed under the microscope. These crystals are never enclosed in the hepatic cellules, but are localised in the extracellular liquid and in the biliary canaliculi; the hydrochlorides of dihydrotoluidine, aselline, and morrhaine can readily be recognised. If the section is moistened with a solution of platinic chloride, and again dried, the acicular crystals of morrhaine platinochloride are formed.

The author uses the term *pangaduine* to denote the mixture of all the alkaloids contained in the oil. This mixture is soluble in alcohol of 80°, in an aqueous solution of glycerol, &c.; it leaves 3·5 per cent. of ash.

Pangaduine is of special value in all maladies characterised by imperfect nutrition: gout, rheumatism, diabetes, neurasthenic weakness, overwork, and all cases where there is abnormal production or elimination of toximes. In tuberculosis, pangaduine stimulates general nutrition, and thus increases the powers of resistance. C. H. B.

Excretion of Ethereal Hydrogen Sulphates in Cholera. By E. BAUMANN (*Zeit. physiol. Chem.*, 17, 511—512).—Pouchet states that the excretion of ethereal sulphates in cholera is at a minimum. Renewed investigation of this point is necessary, taking into account the different stages of the disease. In some stages, the urine certainly contains excess of indican, and in pure cultures of the *Comma bacillus* indole is produced. W. D. H.

A Crystalline Globulin occurring in Human Urine. By D. NOËL PATON (*Proc. Roy. Soc. Edin.*, 19, 102—115).—In the urine of a patient recovering from a prolonged attack of diarrhoea, the percentage of proteïds was found to be very high—2·00 per cent., of which 1·92 consisted of globulin. On another occasion, the total proteïds were 3·82, of which globulin was 3·732. It was obtained by precipitation with ammonium sulphate, filtering, washing, and dialysing; the crystals were elongated and rhombic, and larger than those of tyrosine, but, instead of being acicular, they were terminated by a characteristic angular extremity—coagulation occurs below 60° and above 56°—dried at 110°, they were found to consist of C 51·89 per cent., H 6·88, N 16·06, S 1·24, O 23·93.

The remainder of the paper is of physiological interest only.

E. W. P.

Chemistry of Vegetable Physiology and Agriculture.

Ammoniacal Fermentation in Soils. By A. MÜNTZ and H. COUDON (*Compt. rend.*, 116, 395).—When soil is sterilised by heating at 120°, ammoniacal fermentation is completely prevented. A temperature of 110° is not sufficient to produce this result. The production of ammonia is not due to a single organism, but several bacilli and micrococci, and some moulds, seem to be almost equally effective. It is noteworthy that nitrification, which is beneficial, is brought about by only one organism, whilst ammoniacal fermentation, which as a rule is harmful, can be produced by a comparatively large number of organisms. C. H. B.

The Nitrogen Question. By A. PETERMANN (*Bull. Acad. roy. Belg.* [3], 25, 267—276; compare Abstr., 1890, 816, and this vol., ii, 33).—The object of the experiments described in this paper was to ascertain the effect of sterilisation on nitrogen fixation. The apparatus, of which a sketch is given, consisted of a large inverted bell jar (125 litres capacity) in which two flower pots were placed. The bell-jar was connected with an aspirator. The air before entering the bell-jar passed through cotton wool, and through vessels containing sulphuric acid, and sodium carbonate respectively. There was also an arrangement for boiling the water used for watering. The soil with mineral manure (the same as was used previously, *loc. cit.*) was sterilised by heating for five hours at 150°. The seeds were sterilised by immersion in mercuric chloride solution. The experiments were as follows:—(1) Soil, not sterilised, without higher vegetation, but covered with green and red algæ. (2) Sterilised soil, without vegetation of any kind. (3) Sterilised soil with barley. (4) Soil, not sterilised, with barley (this experiment was lost). (5) Sterilised soil, watered with sterilised water; no cryptogamic vegetation. (6) Soil, not sterilised, watered with rain-water; the soil gradually became covered with lower vegetation.

The numerical results, as regards nitrogen, are next given.

Nitrogen (grams).

	At commencement.			At conclusion.			Gain or loss.
	In soil.	In seed.	Total.	In soil.	In produce.	Total.	
1....	0·0255	—	0·0255	0·0294	—	0·0294	+0·0039
2....	0·0255	—	0·0255	0·0240	—	0·0240	—0·0015
3....	0·0511	0·0573	0·1084	0·0492	0·0575	0·1067	—0·0017
5....	0·0438	—	0·0438	0·0430	—	0·0430	—0·0008
6....	0·0438	—	0·0738*	0·0522	—	0·0769†	+0·0031

* Including 0·0300 gram in rain water added.

† Including 0·0247 gram in drainage.

The results show that barley is not able to fix free nitrogen, and that (as was always maintained by Schloesing) perfectly bare soils are also unable to fix nitrogen. Soils covered with lower vegetation become richer in nitrogen. This explains the previous results with barley (*loc. cit.*); the gain of nitrogen in these experiments was not due, as was then supposed, to fixation by the barley itself, but was brought about by the algæ with which the surface of the sand was more or less covered. Both the earlier, and the new, results are thus in accordance with those of Hellriegel and Wilfarth, and of Schloesing, jun., and Laurent, in showing nitrogen fixation by leguminous plants in symbiosis with nodule organisms, and by lower vegetation, and the absence of such fixation in the case of sterilised soils, and in a non-leguminous higher plant alone.

N. H. M.

Pre-existence of Gluten in Wheat. By BALLAND (*Compt. rend.*, 116, 202—204).—According to Johannsen, no gluten can be obtained from wheat by washing with water at 0°, but the quantity increases with the temperature up to 40°, and then diminishes as the temperature rises. The author finds, however, that gluten can be obtained by treating wheat flour that had been kept for several days at -8° with water at 2°; and experiments made at 2°, 15°, and 60° with the same flour gave respectively 27.0, 27.6, and 30 per cent. of moist gluten. If flour is kept for 36 hours in an atmosphere containing sulphurous anhydride produced by the combustion of 60 grams of sulphur per cubic metre, no gluten can be obtained by the usual method, but it can readily be separated by using water containing salt in solution, or by mixing the flour with a known weight of moist, well-washed gluten, and proceeding in the usual manner.

The author concludes that gluten pre-exists in wheat.

C. H. B.

Proteïds of Linseed. By T. B. OSBORNE (*Amer. Chem. J.*, 14, 629—661).—The paper contains a detailed account of the manner in which the proteïds were separated: for this the original must be consulted. The main results of the experiments were as follows:—Extracts of linseed meal (with water, aqueous sodium chloride, and dilute aqueous potash) contain a globulin precipitable by dialysis; a proteïd, resembling both globulin and albumin, precipitable by long-continued heating at 100°, as well as by sodium chloride in the presence of an acid; proteose and peptone-like substances, and a proteïd not extracted by sodium chloride solution, but soluble in dilute aqueous potash. All attempts to determine the amounts of these various substances failed because of change, while in solution, into non-proteïds. It was further found that the relative amount of the various proteïds was very variable; it is almost certain that the more soluble forms were largely, if not wholly, derived from the globulin in consequence of alteration during extraction and separation. The globulin crystallised in octahedral crystals or in spheroids, and in composition is similar to the globulin of squash seed. It has a tendency to become partially transformed into an "albuminate," which is insoluble in cold sodium chloride solution, but dissolves in dilute sodium carbonate, and also in warm sodium chloride, being reconverted in the last

case into the original globulin. A proteose was obtained resembling closely in composition the deuterovitellose formed when the crystallised vitellin of squash seeds is digested with pepsin-hydrochloric acid.

C. F. B.

Analyses of Kale and Turnip Salad, and Okra. By J. D. TINSLEY (*Amer. Chem. J.*, **14**, 625—626).—The kale and okra pods were weighed immediately after cutting, the turnip salad not until after some hours, when it had wilted somewhat.

100 parts of the "fresh" plant.	Kale salad.	Turnip salad.	Okra pods.
Water by air-drying	88.34	77.78	83.07
Water at 100°	1.32	2.27	1.64
Solid matter	10.34	19.95	15.29
Solid matter containing—			
Pure ash	1.22	2.62	0.91
Ether extract	0.65	1.59	0.29
Crude fibre	1.15	1.57	1.44
Crude starch, gum, &c.	3.43	8.07	10.12
Crude proteïn	3.89	6.10	2.53
Nitrogen, total.	0.62	1.12	0.41
Nitrogen, proteïd	0.25	0.68	0.28

C. F. B.

Analyses of "Black Earth." By F. P. DUNNINGTON and T. C. WHITLOCK (*Amer. Chem. J.*, **14**, 621—623).—The following two analyses are given, one (I) of a soil from the prairie land of Red River, near Winnipeg, Manitoba, the other (II) of Russian tschernozem or black earth from District Balashoff, Government of Saratoff; the two soils are similar in appearance.

Amorph.								
Sand.	SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	TiO ₂ .	CaO.	MgO.	SO ₃ .	CO ₂ .
I. 59.82	5.45	4.00	7.14	0.64	0.61	0.61	0.03	0.37
II. 53.71	12.80	4.13	6.04	0.63	0.75	0.21	0.06	0.02
		P ₂ O ₅ .	K ₂ O.	Organic matter*.	H ₂ O.	Total.		
I.		0.13	1.91	12.49	6.86	99.76		
II.		0.16	1.97	14.91	5.04	100.43		

The two soils are thus similar in chemical composition; they occur in the same latitude, with the same general relief and climate, and have a similar geological history. "May they not therefore be properly considered as of the one variety of soil, 'black earth?'"

C. F. B.

* Contains humus, 0.45 and 0.44, and total nitrogen, 0.44 and 0.31 respectively.

Analytical Chemistry.

Use of Thallium Silver Nitrate for Separating Minerals. By J. W. RETGERS (*Jahrb. f. Min.*, 1893, i, Mem. 90—94).—In an investigation of the isomorphous relations between silver nitrate and the alkali nitrates, the author observed that the double salts of silver nitrate with potassium and ammonium nitrates had very low melting points in comparison with the simple salts. The lowering of the melting point is still more considerable in the case of the thallium double salt, as is shown by the following figures.

	TlNO_3 .	AgNO_3 .	TlAgN_2O_6 .
Melting point.	205°	224°	75°

The remarkable fusibility of this salt, together with its high specific gravity, suggested the possibility of employing it in a molten condition for separating minerals. The results have been found to be thoroughly satisfactory. The sp. gr. of the molten mass is about 5.0, for zircon (sp. gr. 4.5) and braunite (sp. gr. 4.8) float, whilst magnetite (sp. gr. 5.2) sinks. The salt may easily be fused over a water-bath, the result being a colourless, limpid liquid. With this salt, the author has been able to separate from the sand of the Dutch coast a large number of garnets, some zircon crystals, rutile, and magnetite grains.

B. H. B.

Estimation of Precipitates by an Optical Method. By E. AGLOT (*Compt. rend.*, 116, 200—202).—The quantity of precipitate is determined by measuring the length of the column of turbid liquid necessary to cut off the visible form of the brightest part of a flame such as that of a petroleum lamp. The apparatus used is of the same type as a Dubosq colorimeter. In order to keep the precipitate in suspension and secure homogeneity, the liquid is mixed with gum, dextrin, glucose, &c. Constants have, in the first place, to be determined for each substance in various degrees of concentration, and also for each observer.

C. H. B.

Normal Borax Solution. By T. SALZER (*Ber.*, 26, 430; compare Rimbach, this vol., ii, 233).—A question of priority.

Sensitive Litmus Indicator. By J. LÜTTKE (*Zeit. anal. Chem.*, 31, 692).—100 grams of litmus is extracted with warm water, and the extract, concentrated to 200 c.c., is mixed with 20 c.c. of 25 per cent. hydrochloric acid, and dialysed until the acid is removed. The residual colour is extremely sensitive to traces of acid or alkali. By precipitating the concentrated solution with alcohol and drying the precipitate, a solid preparation is obtained which can be kept unchanged for a long time. Another method consists in spreading the solution on glass plates and drying in a stream of carbonic anhydride.

M. J. S.

Quantitative Spectrum Analysis. By G. KRÜSS and H. KRÜSS (*Zeit. anorg. Chem.*, **1**, 104—125).—This paper contains many useful practical details. It is divided into three sections:—1. *Comparison of Various Methods of Quantitative Spectrum Analysis.* 2. *Influence of Temperature on the Absorption Spectrum of Coloured Solutions.* 3. *Improved Form of Vierordt's Spectrophotometer.* A drawing is given of the apparatus described in the third section. A. R. L.

New Direct Separation of Chlorine, Bromine, and Iodine. By P. JANNASCH and K. ASCHOFF (*Zeit. anorg. Chem.* **1**, 144—149 and 245—247).—The authors proceed at first on the same lines as Gooch (*Abstr.*, 1891, 361), thus:—A solution of sodium chloride, potassium bromide, and potassium iodide (about 3 grams of each) is dissolved in water (750 c.c.), acidified with dilute sulphuric acid (*loc. cit.*), and a solution of sodium nitrite (1 gram) in water (10 c.c.) added. Instead of boiling off the iodine and allowing it to escape, a current of steam is passed through the mixture, contained in a specially constructed flask, whereby the liberated iodine is driven off in a quarter of an hour, and is collected as iodide in a second flask containing a mixture of 5 per cent. sodium hydroxide solution (50 c.c.) and 3 per cent. hydrogen peroxide (50 c.c.).

The residual mixture of chloride and bromide is now rendered alkaline, evaporated to about 50 c.c., acidified with dilute (1 : 3) acetic acid (60 c.c.), and a concentrated solution of potassium permanganate (1—1.5 grams) added. A slow current of steam is then passed through, whereby all the bromine (but no chlorine) is driven over in 45 minutes, and may be collected in sodium hydroxide solution. The residual solution containing the chloride is treated with soda and alcohol, and the precipitated manganese oxide filtered off and washed; the three halogens can now be precipitated separately with silver nitrate as usual.

In the second communication, the authors state that when chemically pure acetic acid is employed with their method, the values obtained for bromine are no longer low. A brisk current of steam is passed through the solution containing chlorine and bromine during the distillation, in order to drive over the bromine as quickly as possible; the distillation lasts $1\frac{1}{4}$ hours. The manganese is precipitated from the residual liquid by ammonia and hydrogen peroxide, the precipitate collected and washed with 1 per cent. sodium nitrate solution before determining the chlorine in the filtrate.

A. R. L.

Microchemical Detection of Sulphur. By F. EMICH (*Zeit. anal. Chem.*, **32**, 163—167).—With scarcely an exception, metallic sulphides, when reduced to fine powder, moistened with a solution of calcium chloride, and exposed for a few minutes to the vapours from saturated bromine water, undergo oxidation, resulting in the formation of calcium sulphate, the characteristic crystals of which can be identified by microscopic examination. With a magnifying power of 300 diameters, as little as 0.00002 milligram of sulphur affords distinct indications. Out of 59 mineral sulphides examined, molybdenite alone resisted oxidation obstinately, 20 hours elapsing before

any calcium sulphate crystals could be observed; a momentary roasting, however, accelerated the operation immensely.

For organic sulphur compounds, the reaction is not a general one, although it succeeds with some, such as the thiocyanates, thiourea, mustard seed, and the mustard oils, &c.

M. J. S.

Estimation of Nitrogen in Coal Gas. By C. H. NEW (*J. Soc. Chem. Ind.*, **11**, 415—418).—The method consists in first removing the majority of the bases and certain hydrocarbons, such as benzene and xylene, by passing the gas through concentrated sulphuric acid (sp. gr. 1.85), and then converting the whole of the remaining hydrocarbons into carbonic anhydride and water, by conducting the gas over red-hot copper oxide. The gases which result from this treatment consist of carbonic anhydride and nitrogen, so that the former may be absorbed by soda, and the volume of the remaining nitrogen ascertained.

The apparatus employed consists of the following parts:—1. An apparatus for generating carbonic anhydride. 2. A burette graduated to hold 100 c.c. of gas, fitted at the top with a three-way tap, and connected at its lower extremity with an aspirator. 3. A combustion furnace, containing a combustion tube about 80 cm. long, projecting some 10—12 cm. beyond the furnace, and packed with coarse copper oxide to within 7 cm. of the ends of the tube, which are fitted with india-rubber corks; through each of these a piece of small-bore glass tubing passes, one of these being connected with a small bottle of about 30 c.c. capacity, containing concentrated sulphuric acid. 4. A receptacle for collecting the carbonic anhydride and nitrogen resulting from the combustion of the coal gas, capable of holding 200 c.c., and graduated with a containing mark at 150 c.c. and at 200 c.c. 5. A Hempel's gas apparatus.

The method, which may be carried out in 30 minutes, consists in raising the combustion tube and its contents to a full red heat, during which operation a current of air is aspirated through the tube. The air is then stopped, and a brisk current of carbonic anhydride passed through the sulphuric acid absorber and combustion tube, the generating apparatus having been attached to the latter through the three-way tap. The tube connecting the three-way tap with the absorbing bottle is now closed by a pinch-cock, and the gas receiver, having been filled completely with mercury, is connected with the other end of the combustion tube, taking care to avoid the entrance of any air. The pinch-cock intervening between the carbonic anhydride generator and the three-way tap is also closed. The india-rubber tube connecting the absorption bottle with the three-way cock is then temporarily removed, and after displacing all air in the burette with mercury, coal gas is admitted by connecting with the gas supply and lowering the aspirator bottle, the gas being adjusted to the 100 c.c. mark by levelling the height of the mercury. The absorption bottle is now again connected with the three-way tap, and the pinch-cocks both here and at the top of the receiver are opened. The gas is then slowly chased over from the burette through the absorption bottle and the combustion tube, the rate at which the gas is passing being

ascertained by observing the bubbles in the absorber. The displacement of the 100 c.c. of gas should occupy about 15 minutes. The connection with the burette is then closed, and the tap once more connected with the carbonic anhydride generator, from which a current of gas is slowly passed through the whole apparatus, displacing the coal gas in the absorber, and carrying over all the nitrogen in the combustion tube into the receiver. The mercury in the receiver is brought nearly to a level during the experiment, maintaining the gas, however, under a slight pressure, and adjusting the same by means of the small tap at the bottom, so that when the gas reaches the 150 c.c. mark, and the pinch-cock at the top and the tap at the bottom are simultaneously closed, the levels of the two columns of mercury are coincident with each other. The receiver is then disconnected, and the combustion tube having been opened to the air, the pump is again started to reoxidise the copper oxide. The wide mouthed limb of the receiver is then filled with mercury, and 100 c.c. of the gas passed into the Hempel burette, the carbonic anhydride being absorbed with soda in the usual way. It has also been found necessary to remove traces of oxygen from the gas before taking the final reading of the nitrogen. The volume of the remaining gas is then noted, calculated to 150 c.c., and after correction for temperature and pressure gives the volume per cent. of nitrogen.

D. B.

Dumas' Method of estimating Nitrogen in Organic Substances. By J. O'SULLIVAN (*J. Soc. Chem. Ind.*, 11, 327—328).—The author's experience with the absolute method of Dumas proves that the gas obtained invariably contains an appreciable quantity of nitric oxide, and that the amount is not much influenced by the presence of the usual copper in the combustion tube. By discarding the copper, and substituting a plug of asbestos, not much more nitric oxide is found in the gas. This does away with the tedious process of reducing the oxidised copper. As there is always nitric oxide in the gas, more accurate results are obtained by measuring the quantity of nitric oxide and nitrogen by means of a gas analysis apparatus.

D. B.

Stock's Process for the Estimation of Nitrogen. By W. F. K. STOCK (*Analyst*, 18, 58, and 58—60).—The author (compare Abstr., 1892, 1592) has dispensed with one of the bunsen burners. The apparatus has been simplified, and now consists of a 150 c.c. Wurtz flask, the tube of which runs into the condenser, and is kept at boiling point by the ammoniacal steam from the distilling flask. Not a trace of sodium hydroxide finds its way into the distillate.

The author, in the second paper, defends his process against an attack made on it by Skertchly, who does not seem to have strictly followed the directions given.

L. DE K.

Estimation of Nitric acid by means of Cinchonamine Salts. By P. GAMMARELLI (*Gazzetta*, 22, ii, 635—642).—Arnaud's method of estimating nitric acid (Abstr., 1884, 87), based on the sparing solubility of cinchonamine nitrate, is of little value. 100 parts of a

saturated aqueous solution contain 0.21 part of the salt at 11.5°, so that a loss of 3 per cent. or so is incurred, even when the minimum quantity of liquid is employed in the analysis. The solubility of the salt remains practically the same when a 1 per cent. aqueous solution of potassium sulphate or chloride is used in place of water. The *nitrite* forms small prisms, which melt at 174° with decomposition; it is more soluble than the nitrate, 100 parts of its saturated aqueous solution containing 0.52 part of the salt at 10.4° and 0.63 part at 13.8°.

W. J. P.

Reaction of Nitrites, and its Applications. By C. M. VAN DEVENTER (*Ber.*, 26, 589—593).—Schäffer pointed out long ago that an intensely yellow liquid is obtained when a few drops of potassium ferrocyanide and then a little acetic acid are added to a very dilute sulphuric acid solution of potassium nitrite. The author finds that the action in this case is expressed by the equation $2K_4Fe(CN)_6 + 2HNO_2 + 2C_2H_4O_2 = K_6Fe_2(CN)_{12} + 2KC_2H_3O_2 + 2NO + 2H_2O$, and that even in the cold the formation of nitric oxide takes place quantitatively, so that the reaction can be made use of not only for the preparation of nitric oxide, but also for the detection and estimation of nitrous acid.

For preparing nitric oxide, a mixture of solutions of potassium ferrocyanide and potassium nitrite is gradually added from a stoppered funnel to a flask containing acetic acid; the contents of the flask must be vigorously shaken during the operation.

Nitrous acid can be detected, even in presence of nitric acid, which is without influence, by the evolution of nitric oxide which takes place on mixing the above-mentioned solutions, provided that the quantity of nitrite is not so small that the whole of the gas remains in solution; a feeble, and only a momentary, gas evolution is observed when about 4 milligrams of potassium nitrite are present in every 20 c.c. of the mixture of the three solutions.

The estimation of nitrous acid can be conveniently carried out as follows. A eudiometer, provided with a stopcock, is completely filled with an approximately 14 per cent. solution of potassium ferrocyanide, and the open end is then dipped vertically into a vessel containing the same liquid; the nitrite solution is introduced with the aid of a funnel attached to the upper end, the funnel being washed first with a little water, then with acetic acid, and finally with a small quantity of concentrated potassium ferrocyanide. As soon as the gas evolution begins to slacken, the eudiometer is vigorously shaken, the open end being kept dipped into the solution of potassium ferrocyanide, until the level of the liquid in the eudiometer remains stationary. Water is then slowly introduced at the top with the aid of a funnel, and, as soon as the potassium ferrocyanide solution has been almost completely displaced, the open end is closed with the thumb and the tube vigorously shaken; it is then dipped into the potassium ferrocyanide solution, and, after some time, the volume of the nitric oxide is observed. The usual corrections are made for temperature and pressure, and also for the quantity of gas which has been dissolved by the water in the apparatus. Quantitative

experiments gave results agreeing with one another, and also with those obtained by Péan de St. Gilles' method, so that, in case standard solutions are not at hand, the direct measurement of the gas in the manner described may be recommended as a convenient method for the estimation of nitrous acid.

F. S. K.

Spica's Process for the Estimation of Phosphoric acid.

By C. ARNOLD and K. WEDEMEYER (*Zeit. angew. Chem.*, 1892, 603—604).—Spica estimates the amount of phosphoric acid in basic slags by heating them with strong sulphuric acid, and then extracting the mass with a large quantity of absolute alcohol to dissolve the phosphoric acid. After the alcohol has been expelled, the liquid is neutralised and titrated with a standard solution of potassium ferric sulphate with salicylic acid as indicator. The authors have investigated the process, but cannot recommend it. A sample which gave 17·88 per cent. of phosphoric acid by the molybdate process only gave 16·59 per cent. by titration.

L. DE K.

Separation and Estimation of Pyrophosphoric and Metaphosphoric acids. By G. v. KNORRE (*Zeit. angew. Chem.*, 1892, 639—641).—Estimation of Pyrophosphoric acid.—Acid sodium pyrophosphate ($\text{Na}_2\text{H}_2\text{P}_2\text{O}_7 + 6\text{H}_2\text{O}$) is neutral towards methyl-orange and tropæolin. If, therefore, hydrochloric acid is added to a solution of normal sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 + 10\text{H}_2\text{O}$), the end reaction will only make its appearance when all the normal pyrophosphate has changed into the acid salt. The test analyses are satisfactory.

A solution of normal sodium pyrophosphate is strongly alkaline towards phenolphthalein. If, therefore, a solution of the acid phosphate is titrated with potash, the results will be too low, as the end reaction already shows long before the acid salt has become neutralised. The author has, however, succeeded in getting good results by titrating with lime-water in presence of calcium chloride, which precipitates the normal salt and so removes the alkalinity. If a solution contains both acid and normal pyrophosphates, the latter may be estimated by means of methyl-orange and standard acid. The total amount of phosphate may then be determined by means of calcium chloride and standard lime-water with phenolphthalein as indicator.

To detect pyrophosphoric acid in presence of the meta-acid, the author recommends the addition of zinc acetate to the perfectly cold solution, which will precipitate the least trace of the pyro-compound; but attempts to render this a means of quantitative estimation proved unsuccessful.

L. DE K.

Estimation of Arsenic. By H. BÄCKSTRÖM (*Zeit. anal. Chem.*, 31, 663—665).—The author advocates the weighing of arsenic as pentoxide after precipitation as sulphide. The solution containing the arsenic is treated with hydrogen sulphide, first at the ordinary temperature and then on the water bath. It is immaterial whether the precipitate is trisulphide or pentasulphide, or contains free sulphur. After complete washing, it is rinsed from the filter into a beaker, any particles adhering to the filter being dissolved by am-

monia. After drying on the water bath, it is oxidised by repeated careful additions of rectified fuming nitric acid in small portions. When the sulphur is wholly oxidised, the liquid is transferred to a platinum crucible, and, after evaporation, is heated to a temperature just short of redness to expel sulphuric acid, the last traces of which are somewhat stubbornly retained. Complete deprivation can, however, be attained without decomposition of the arsenic pentoxide, which is stable at temperatures below a red heat. Being hygroscopic, it must be weighed with rapidity. The results are as accurate as can be desired.

M. J. S.

Estimation of Silica in Clay. By L. ARCHBUTT (*J. Soc. Chem. Ind.*, 11, 215—217).—Craig (Abstr., 1890, 194) states that by fusing pure silica or siliceous material with alkali carbonates, not more than 97.5 per cent. of the silica can be found in the insoluble residue, and this statement has led Gilbert (Abstr., 1890, 1026) to make a number of experiments, which show that in the analysis of silicates containing alumina, but practically free from lime and magnesia, dehydration, even at 280°, will not prevent some milligrams of the silica from passing into the filtrate, so that in accurate analyses the silica in the filtrate must always be recovered. From the author's experiments, it appears almost hopeless to obtain by a single dehydration the whole of the silica, and the following process has been adopted as being more trustworthy. 1 gram of the finely-powdered clay is fused with 5 grams of pure, mixed alkali carbonates. The mass is extracted with about 200 c.c. of water, the solution acidified with hydrochloric acid in good excess, and evaporated to dryness on the steam bath in a porcelain dish, reducing the residue to small grains. It is then heated in an air oven at 150° for one hour, dissolved in hydrochloric acid and water, filtered, and the silica washed. The filtrate is evaporated with 20 c.c. of strong sulphuric acid until fumes are evolved very strongly. The residue is then dissolved in hydrochloric acid and water, and the additional small quantity of silica collected and washed. The mixed residues are ignited at the highest temperature of the muffle until constant in weight. The silica is then volatilised with hydrofluoric acid and a few drops of sulphuric acid, and the residue ignited until constant in weight. The difference is pure silica.

D. B.

Estimation of Potassium. By E. W. HILGARD (*Zeit. anal. Chem.*, 32, 184—185).—The platinochloride is decomposed by ignition in a platinum crucible, the lower half of whose inner surface has previously been covered with a layer of platinum sponge by strong ignition of some of the double salt. The presence of the sponge greatly facilitates the decomposition at even a moderately low temperature. When decomposition is complete, the crucible is strongly ignited for some time. This consolidates the reduced platinum, thus preventing loss when washing out the soluble matters. A little hydrochloric acid is then warmed in the crucible, and if it acquires a yellow colour, the ignition is repeated with the addition of oxalic acid. The soluble matters are then washed out with acidified boiling water, and the residual

platinum is weighed. Since the washing usually removes some sodium chloride and traces of earths, together with silicates, from the filter ash, the results are lower and more accurate than those from weighing the double salt.

M. J. S.

Detection of Ammonia with Nessler's Reagent. By L. L. DE KONINCK (*Zeit. anal. Chem.*, **32**, 188).—An alcoholic solution of ammonia gives neither precipitate nor coloration with Nessler's reagent. Alcohol does not, however, hinder the reaction of ammonia with mercuric chloride (Bohlig's test).

M. J. S.

Separation of Strontium from Calcium. By R. FRESENIUS (*Zeit. anal. Chem.*, **32**, 189—203).—Rose's method of digesting the sulphates with a strong solution of ammonium sulphate, Fleischer's method of boiling the oxalates with potassium sulphate, and Sidersky's methods of precipitation with a mixture of ammonium sulphate and oxalate are all subject to the same defect of affording only approximately correct numbers as the result of compensating errors. In all cases each of the separated constituents is found to be largely contaminated with the other. Stromeyer's method, as improved by Rose, which consists in the treatment of the anhydrous nitrates with a mixture of equal volumes of absolute alcohol and ether, affords an almost perfect separation. When very carefully dried at 130°, 1 part of strontium nitrate requires 83,044 parts of the ether alcohol for solution, whilst 1 part of calcium nitrate dissolves in 1·87 parts. The following mode of conducting the separation yields excellent results. The nitrate solution is evaporated in a small porcelain basin and dried for a long time at 130°. The residue is rubbed to powder and rapidly treated, with rubbing, five times with 5 c.c. of the ether alcohol, pouring the solution into a small flask. The residue in the basin is dissolved in water, re-evaporated, and dried at 130°, rubbed to powder, and transferred as completely as possible to the flask, the basin being thrice rinsed with 5 c.c. of the ether alcohol. The flask is then frequently shaken during 24 hours, and the solution of the calcium nitrate filtered through a small filter, washing the residual strontium nitrate and the filter by 12 decantations with 5 c.c. of ether alcohol each time. In a separation reported, the strontium came out 0·17 per cent. too high, and the calcium 0·56 per cent. too low, and spectral analysis showed only traces of each metal in the precipitate of the other.

M. J. S.

Volumetric Determination of Calcium Phosphate by means of Uranium Solution. By J. B. COLEMAN and J. D. GRANGER (*J. Soc. Chem. Ind.*, **11**, 328—329).—It is stated by some authorities that in estimating calcium phosphate by means of uranium solution, correct results are only obtainable when the solution is standardised with calcium phosphate in the place of sodium phosphate. This statement is confirmed by the authors, who found the results were otherwise low, especially in cases where the proportion of calcium phosphate was considerable. It is also necessary to estimate the percentage of

phosphoric acid in the calcium phosphate used for standardising by the gravimetric method. D. B.

Volumetric Estimation of Lead. By F. C. KNIGHT (*Chem. News*, 67, 128—129).—The author, having satisfied himself that lead oxalate is practically insoluble under the conditions involved, has adopted the following method for estimating lead for technical purposes. The lead (0.05—0.5 gram), if necessary, having been reduced to the metallic state, is dissolved in 3 c.c. of concentrated nitric acid, diluted with 10 c.c. of hot water, and precipitated with slight excess of sodium carbonate. The precipitate is dissolved in 5 c.c. of strong acetic acid, the solution mixed with 20 c.c. of 95 per cent. alcohol, heated to 65°, and the lead precipitated by adding 10 c.c. of a saturated solution of oxalic acid. This precipitate, after washing thoroughly with hot water, is placed in a beaker with 50 c.c. of hot water, and 5 c.c. of concentrated sulphuric acid is added. The solution is warmed to 65°, and the liberated oxalic acid titrated with standardised permanganate. D. A. L.

Estimation of Oxygen in Lead. By G. LUNGE and E. SCHMID (*Zeit. anorg. Chem.*, 2, 451—460).—The authors find that lead usually contains but a very minute trace of oxygen, about 0.0025 per cent., but that when the lead is contaminated with from 0.01 to 1 per cent. of copper the quantity of oxygen is much increased. A special form of apparatus was employed for passing hydrogen over the heated lead and absorbing the water formed. G. T. M.

Gravimetric Estimation of Zinc as Sulphide. By W. F. LOWE (*J. Soc. Chem. Ind.*, 11, 131—133).—The usual method of estimating zinc in blende and other ores of zinc by a standard solution of sodium sulphide, although fairly rapid and sufficiently accurate for many purposes, cannot be considered a very satisfactory process. The gravimetric method is very little used, owing to the supposed difficulty of filtering zinc sulphide; but if the necessary precautions are taken, very little difficulty will be experienced and very accurate results obtained. 1 gram of the dried and finely-ground sample is placed in a conical flask, 10—15 c.c. of strong hydrochloric acid added, the flask covered with a small funnel, and boiled on an iron plate until dissolved. Two or three drops of strong nitric acid are then added to ensure the complete solution of the ore. This addition should not, however, be made until the solvent action of the hydrochloric acid is complete, as otherwise a separation of sulphur takes place. As soon as all the nitrous fumes have passed off, the solution is diluted to about 100 c.c. with cold water, and a good stream of hydrogen sulphide passed through until the precipitate turns black and settles readily. It is then filtered through a covered filter, and washed with water containing a little hydrogen sulphide. The solution is then heated in an uncovered beaker on the iron plate to a temperature just below boiling. As soon as the hydrogen sulphide has passed off, some bromine water is added to oxidise the iron, the solution cooled, and an excess of ammonia is added. It is allowed to stand for a few minutes on the iron plate, and filtered.

The precipitate is washed slightly, and is then redissolved in warm hydrochloric acid, reprecipitated with ammonia, filtered through the same paper, and washed with hot water containing a little ammonia. The solution is made up with hot water to about 750 c.c., and is heated in a conical flask nearly to boiling. About 10 c.c. of freshly-prepared, colourless ammonium sulphide is added, and the solution boiled for two or three minutes and allowed to settle. The boiling converts the slimy precipitate into a granular one. The flask is then covered and left to stand all night, the clear liquid is siphoned off to just above the precipitate, and this portion, although having only a slight opalescence, is filtered through a double filter of good Swedish filter-paper, and it is important that the filter should exactly fit the funnel, and be held down in its place whilst it is moistened before use. After the decanted portion has been filtered, the precipitate is washed once by decantation with hot water containing a little ammonium chloride and a few drops of ammonium sulphide. It is transferred with hot water, containing a few drops of ammonium sulphide, to the filter, which is kept covered with a ground glass plate. The precipitate is then dried, transferred to a Rose's crucible, the filter being burnt in a separate crucible, and the ash added to the precipitate, a little pure sulphur is added, and the whole ignited in a current of coal-gas, at first gently and then for about five minutes in a large Bunsen flame. After cooling in the current of coal-gas, it is weighed. The results quoted show the process to be very accurate.

If the ores contain manganese, the process requires to be modified; the zinc can be precipitated as sulphide in an acetic acid solution, or the manganese can first be removed by precipitation with bromine.

D. B.

Volumetric Estimation of Zinc. By B. C. HINMAN (*Chem. News*, 67, 30—32).—Preliminary experiments proved that Von Schulz and Low's method of determining zinc, whilst satisfactory for readily decomposable ores containing little or no iron, requires modification under other circumstances, inasmuch as the iron precipitate carries zinc down with it; manganic oxide, however, does not behave in this manner. The modified method is as follows:—The very finely-pulverised ore is treated with nitro-hydrochloric acid, either until decomposition is complete or until action ceases; if decomposition is then incomplete, the mass is taken to dryness, heated to dehydrate the silica, and then treated with dilute hydrochloric acid; the insoluble residue is fused with sodium carbonate and nitrate, dissolved in hydrochloric acid, and added to the other solution, which is now boiled with nitric acid until all the hydrochloric acid is expelled, then taken nearly to dryness, and, after the addition of the usual quantity of nitric acid, saturated with potassium chlorate, and evaporated to total dryness. The dry residue is treated with ammonium chloride and ammonia, the solution diluted, and heated to boiling; the precipitate is collected, washed with weak ammonium chloride rendered alkaline with ammonia, then dried, and re-treated with the chlorate mixture. The solutions are then mixed and acidified to the same degree as that employed when standardising; to effect this, a small

quantity of an indicator is added to the solution, and, after neutralising, the measured quantity of acid is run in. The acidified solution is heated to boiling, and titrated with ferrocyanide. D. A. L.

Separation of Iron from Aluminium. By H. BORNTÄGER (*Zeit. anal. Chem.*, **32**, 187).—After weighing the ignited oxides, they are dissolved in hydrochloric acid, and potash (not soda) added until the solution is nearly neutral. The oxides are then precipitated hot by neutral potassium oleate, avoiding excess. The precipitate is washed on a filter with hot water, and after drying over calcium chloride until most of the water is removed, it is treated with hot petroleum, which dissolves the ferric oleate. The residual aluminium oleate is ignited, and leaves alumina as a porous, white mass. The filtrate can be evaporated and ignited in a platinum basin so as to weigh the ferric oxide. Ferrous oxide may be separated from alumina by the same treatment without oxidation. The results are very exact. M. J. S.

Estimation of Manganese in Iron. By M. A. v. REIS (*Zeit. angew. Chem.*, 1892, 604—607; 672—674).—Of the numerous processes recommended from time to time, the author prefers the following:—About 1 gram (or more) of the sample is dissolved in 25 c.c. of an acid mixture containing 275 vols. of water, 125 vols. of nitric acid (sp. gr. 1.4), and 100 vols. of strong sulphuric acid. The mixture is heated over a naked flame, and evaporated until sulphuric fumes escape. After cooling, the liquid is diluted to about 100 c.c. with water, another 10 c.c. of the acid is added, and the mixture heated until the salts have dissolved. To destroy any carbon, the solution is introduced into a 1 litre Erlenmeyer flask, and boiled for four minutes with 3 grams of barium peroxide and 5 c.c. of nitric acid. 400 c.c. of boiling water is next added, then a sufficiency of an emulsion of zinc oxide (20 grams of ZnO generally suffices), and the manganese may then at once be titrated with a standard solution of potassium permanganate.

From the author's test analyses, it appears that the accuracy of the process is not influenced by the amount of acid or zinc oxide used, provided these substances are free from manganese and not used in inordinately large quantities. L. DE K.

Analysis of Ferrosilicon and Siliceous Spiegel. By T. W. HOGG (*Chem. News*, **67**, 27—28).—It is pointed out that the impression that high-percentage ferrosilicon and siliceous spiegel is very imperfectly attacked by nitrohydrochloric acid is a misconception, arising, firstly, from comparatively coarse particles becoming covered with a protective coating of silica, and, secondly, from the silica retaining iron oxide, which it takes up during the dry heating usually practised subsequent to the treatment with the acid. The first obstacle can be removed by grinding the portion of alloy intended for analysis to extreme fineness in an agate mortar, whilst the second may be avoided by filtering off the silica and graphite after the treatment with acid, and evaporating the filtrate to dryness by itself, in order to obtain the small quantity of dissolved silica. When titanite oxide is

present, and great accuracy is required, treatment with sulphuric and hydrofluoric acid would be adopted. D. A. L.

Decomposition of Tin Slags by the Fluoride Method. By H. N. WARREN (*Chem. News*, 67, 16).—The following method is not only rapid, but also eliminates risk of loss by volatilisation. The pulverised slag is gently heated, for a few moments, on a sand-bath, in a platinum vessel, with a mixture of equal parts of hydrofluoric and hydrochloric acids; the solution is diluted to a known volume; half of it is precipitated with hydrogen sulphide, and the precipitated mixed sulphides of tin and antimony, after purification by redissolving, &c., if necessary, are ignited and weighed as oxides. The other half is rendered alkaline with ammonia, excess of oxalic acid is added, and by means of hydrogen sulphide the antimony sulphide is now precipitated alone, and is ignited and weighed. The percentage of tin is readily ascertained by deducting this weight from that of the mixed oxides. D. A. L.

Quantitative Analysis by Electrolysis. By F. RÜDORFF (*Zeit. angew. Chem.*, 1892, 695—698).—Estimation of *Gold*.—The author (compare this vol., pp. 93—95) dissolves a few grams of potassium cyanide in water contained in a platinum dish, the inside of which is coated with silver. The gold solution, which should contain no more than 0.3 gram of the metal, is now added, and the mixture is diluted to about 120 c.c. Two or three Meidinger cells are used, and the gold is deposited as a lustrous, smooth, adherent mass, which may afterwards be readily removed by warming with nitric acid.

Estimation of Platinum.—The solution should contain no more than 0.5 gram of the metal. After adding five drops of 10 per cent. sulphuric acid, and diluting to 120 c.c., the platinum is completely precipitated by electrolysis with two cells. If the basin is afterwards well rubbed with sand, the metal becomes smooth and lustrous, and the dish will have increased in value.

Separations: Copper from Silver.—The total amount of metal should not exceed 0.5 gram. If the amount of copper is about equal to or less than the silver, the neutralised solution is mixed with 8 grams of potassium cyanide, diluted to 120 c.c., and electrolysed with two or three cells. After 12 hours, the silver will have separated out completely, and is free from copper. The liquid is evaporated to dryness after the addition of sulphuric acid, the residue is dissolved in water, and mixed with 3 grams of ammonium nitrate and 20 c.c. of ammonia (sp. gr. 0.91). After diluting to 120 c.c., the solution is electrolysed by means of four or five cells, and the precipitated copper is treated as previously directed.

Copper from Mercury.—The solution should contain about 0.4 gram of metal. If the amount of copper is less than the mercury, 6 grams of potassium cyanide is added, the whole diluted to 120 c.c., and electrolysed with two or three cells. If, however, the copper preponderates, 10 grams of potassium cyanide should be added. The mercury separates within 12 hours, and the copper is afterwards estimated as directed.

Copper from Cadmium.—The author recommends dividing the solution into two parts, and precipitating the copper in the one, and the cadmium in the other. The solution, which should not contain more than 0.5 gram of metal, is mixed with 2 c.c. of nitric acid (sp. gr. 1.2), and after being diluted to 120 c.c., electrolysed with 3–4 cells. The precipitated copper is perfectly free from cadmium. The other portion is mixed with 12 grams of potassium cyanide and electrolysed with three cells. Cadmium, free from copper, is deposited.

Copper from Nickel.—The solution, which should contain no more than 0.5 gram of metal, is mixed with 1 c.c. of nitric acid, diluted to 120 c.c., and electrolysed with three cells. The copper deposit is treated with the usual precautions, and the liquid contains the nickel, which may be recovered by electrolysing with four or six cells, after the addition of 20 c.c. of a saturated solution of ammonium sulphate and 25 c.c. of ammonia; but the author generally works as follows:—An aliquot part of the original solution is acidified with three drops of sulphuric acid, and the copper is precipitated by hydrogen sulphide. The filtrate, after the addition of 20 c.c. solution of hydrogen peroxide, is evaporated to about 60 c.c., mixed with ammonium sulphate and ammonia, and then electrolysed.

L. DE K.

Supersaturation of Solutions of Oxygen in Water. By C. A. SEYLER (*Chem. News*, 67, 87).—Experiments made with the water of the Swansea supply, which is soft and organically pure, show that the temperature may be raised from 1° to 9.5°, or from 13° to 26.5°, without noticeable effect on the dissolved oxygen, the gaseous solution remaining supersaturated until shaken vigorously, when it parts with its excess of oxygen.

D. A. L.

Source of Error in the Ultimate Analysis of Organic Substances. By G. S. JOHNSON (*Chem. News*, 67, 99).—Neumann's observations concerning the hydrogen occluded by copper turnings on the results of hydrogen estimations confirm those published by the author (this Journal, 1876, i, 178, and Trans., 1879, 232). The author obviates this error by selecting copper as free from sulphur as possible; by alternately oxidising and reducing the copper many times before using, and by adopting the following arrangement and procedure in the combustion: the reduced copper for the reduction of the nitrogen oxides is placed in the front part of the tube and is followed in backward order by granulated copper oxide, a boat with the substance, a second boat with reduced copper, and a third boat with fused potassium chlorate. The whole is heated to redness, except the boats containing the substance and the chlorate, and before adjusting the weighed apparatus in front, a slow stream of dried air is passed, until the copper behind the substances is oxidised. The combustion is then proceeded with.

D. A. L.

Detection of Nitrobenzene. By J. MARPURGO (*Zeit. anal. Chem.*, 32, 235; from *Pharm. Post*, 23, 258).—In a porcelain basin are placed two drops of liquid phenol, three drops of water, and a fragment of potash, as large as a pea. The mixture is boiled, and the aqueous solution to be tested is added. On prolonged boiling, nitro-

benzene produces at the edges of the liquid a crimson ring, which, on addition of a solution of bleaching powder, turns emerald-green. To examine a soap, it is dissolved in water, treated with excess of milk of lime, extracted with ether, and the residue of the ethereal solution tested as above. Oil of bitter almonds, warmed with manganese peroxide and sulphuric acid, loses its characteristic odour, whilst that of nitrobenzene remains unaffected. M. J. S.

Analysis of Creosotes. By A. BÉHAL and E. CHOAY (*Compt. rend.*, 116, 197—200).—See this vol., i, 320.

Gas-volumetric Estimation of Organic Acids. By H. KUX (*Zeit. anal. Chem.*, 32, 129—163).—The author has investigated the conditions under which the commoner organic acids can be estimated by Baumann's gas-volumetric iodine process (*Abstr.*, 1892, 539). The general conditions essential to success are purity of the reagents, an approximate adjustment of the proportions, as, for example, for an evolution of 50 c.c. of oxygen there should be used about 2 grams of potassium iodide, 0.2 gram of iodate, not more than double the theoretical quantity of hydrogen peroxide, and between twice and ten times the theoretical amount of potash (solution of 1 part potassium hydroxide in 1 part of water), and lastly, extreme rapidity in mixing the iodine solution with the alkaline hydrogen peroxide. The apparatus used was Wagner's modification of Knop's azotometer, the reaction vessel consisting of a flask with a short, wide tube, fused to its bottom. In the outer chamber are placed the iodide, iodate, and acid to be estimated, diluting the whole to between 40 and 50 c.c. In the tube is placed a cooled mixture of 2—3 c.c. of hydrogen peroxide (2—3 per cent.) and 4 c.c. of the potash. After equalisation of temperature, the liquid in the flask is brought into rotation, and the contents of the tube suddenly mixed with it by inclining the flask, but without stopping the rotation. The whole reaction is over in 15 seconds, and after 10 minutes' cooling the volume of oxygen is read off.

The action of the organic acids on the iodide and iodate is in most cases slower than that of mineral acids. It can be accelerated by heat, in which case the mixture should be enclosed in a well-stoppered bottle, and plunged into water of 70—80°. Formic acid requires a digestion of half an hour in the cold, heating or longer digestion being inadmissible. Acetic acid requires two hours in the cold, or 10—15 minutes at 70°. Tartaric and citric acids require three hours in the cold, or 10—15 minutes at 70°. Propionic acid, three hours cold, or one hour hot. Malic acid, four hours cold, or 10—15 minutes hot. Butyric and succinic acids, 12 hours cold, or half an hour hot. Oxalic acid, lactic acid, and potassium hydrogen oxalate act instantly without heat, and potassium hydrogen tartrate requires 10—15 minutes at 70°. Iodic acid can be estimated by the same method, a small excess of a mineral acid being employed to liberate it. M. J. S.

The Reichert Process. By H. D. RICHMOND (*Analyst*, 18, 64—65).—Wilson has shown that the rate of distillation of dilute

acetic acid is influenced by the salts in the solution distilled, and argues from the analogy between acetic acid and the acids from butter, that, therefore, the Reichert distillation process must be inaccurate.

The author replies that, however scientifically correct Wilson's views may be, in practice, the error is quite negligible.

L. DE K.

Estimation of Insoluble Fatty Acids. By C. E. CASSAL (*Analyst*, 18, 44—45).—The use of a filter in the process of washing insoluble fatty acids in butter or other fats being cumbrous and liable to introduce errors, the author prefers to wash these acids in a globular separator made of thin glass, which will stand boiling water.

L. DE K.

Preservation of Milk for Analysis. By J. A. ALÉN (*Bied. Centr.*, 1892, 549—550).—It is frequently more convenient to analyse several samples of milk as one, and to enable this to be done without the milk turning sour, after being kept for days, potassium dichromate is to be added. The milk will then remain good, and further samples may be added to the first day after day. Five grams is sufficient for 250—500 c.c. of milk, the mixture being preserved in closed vessels at a temperature not exceeding +50°. This method, which the author intends patenting, allows of an accurate average composition being obtained.

E. W. P.

Leffmann and Beam's Method of Estimation of Milk Fat. By H. D. RICHMOND (*Analyst*, 17, 144—152).—The author has made a thorough mathematical and chemical investigation of this process (*Abstr.*, 1892, 1532), and thinks it may be classed among the trustworthy methods.

A source of error, although inappreciable, may be introduced by the presence of lactic acid.

L. DE K.

Estimation of Fat in Milk. By L. LIEBERMANN and S. SZÉKELY (*Zeit. anal. Chem.*, 32, 168—173).—It was pointed out in 1885 by one of the authors (*Pharm. Centralhalle*, 1885, 253) that ether extracts from milk other substances besides fat. The residue from the evaporation of the ethereal solution is no longer wholly soluble in ether, and the results of extraction with light petroleum are always lower than those with ether. The following method, which is very rapid, gives results differing only in the second decimal from those obtained by complete exhaustion with petroleum. 50 c.c. of milk, at the temperature of the laboratory, is placed in a cylinder 25 cm. high and of 4.5 cm. diameter. 5 c.c. of potash (sp. gr. 1.27) is added, and, after inserting a cork, the whole is well shaken. There is next added 50 c.c. of light petroleum (sp. gr. 0.663 and boiling at about 60°), and the mixture is shaken until an emulsion forms. 50 c.c. of 96 per cent. alcohol is then added and again shaken. In four or five minutes, the petroleum will have completely separated. The shaking is repeated at least three times, for a quarter of a minute each time, and with sufficient intervals for complete separation. 20 c.c. of the petroleum layer is now withdrawn by a pipette and evaporated in a tared

vessel, drying the residue at 110—120°. The weight, multiplied by 5, and corrected for the specific gravity of the milk, gives the percentage of fat.

M. J. S.

Iodine Absorption. By F. GANTTER (*Zeit. anal. Chem.*, **32**, 178—181 and 181—184).—In order to investigate the influence which the addition of mercuric chloride in Hübl's process has on the absorption of iodine by unsaturated fatty substances, the author employed a solution of iodine in carbon tetrachloride, and dissolved the fat directly in the iodine solution after the addition of varying quantities of mercuric chloride. Under these conditions, the percentage of iodine absorbed by linseed oil rises with the increase in the amount of mercuric chloride, being, when the excess of iodine was small, 83·5 per 100 parts of oil when the mercuric chloride was 50 per cent., and 148 per 100 when the amount of mercuric chloride was increased tenfold. With a large excess of iodine, a similar variation took place, as much as 188 per cent. being absorbed when 6 parts of iodine and 10 of mercuric chloride were employed for 1 part of oil, and at the same time the percentage absorption varied with the amount of iodine used, when the mercuric chloride was kept constant. Lard exhibited similar phenomena, and even saturated compounds, such as lauric and stearic acids, which in the absence of mercuric chloride absorb no iodine, show, when mercuric chloride is added, a small absorption, rising with increased amounts of mercuric chloride. In conducting Hübl's process, it is therefore necessary that the conditions be kept absolutely constant, and even then the results have only a relative value.

In order to avoid the complications introduced, and the excessively high results obtained, by the addition of mercuric chloride (see above), it is necessary to employ a menstruum in which both iodine and fats are freely soluble. Carbon tetrachloride fulfils these requirements. With small excesses of iodine, the absorption is extremely sluggish, but by employing 4 or 5 parts of iodine for 1 part of fat, the absorption is complete in about 50 hours, and concordant results are obtained. The iodine solution recommended contains 10 grams per litre. In making this solution, the iodine should not be dissolved in the graduated flask itself, since the opacity of the liquid does not allow of ascertaining when solution is complete. The iodine solution is titrated by one of sodium thiosulphate containing 19·528 grams per litre, the two solutions being shaken together in a well-stoppered bottle, with starch indicator towards the end.

Of drying oils 0·1 gram, of other fats 0·2 gram, is weighed into a stoppered bottle; 50 c.c. of the iodine solution is added, and the mixture shaken until the oil is completely dissolved. Sufficient water is then added to form a layer several millimetres thick on the surface, the stopper is inserted, and the whole allowed to react at the ordinary temperature for 50 hours. The residual iodine is then titrated as before. At lower temperatures, higher numbers are obtained, and conversely. A single estimation of the iodine absorption of linseed oil reported shows only 76·2 per cent.

M. J. S.

Contributions to the Analysis of Fats. By J. LEWKOWITSCH (*J. Soc. Chem. Ind.*, 11, 134—145; compare *Abstr.*, 1891, 509, and 1892, 544).—*Sperm Oil*.—The higher alcohols contained in sperm oil were prepared in the usual way by saponifying a pure specimen of the latter with alcoholic potash, when 41 per cent. of unsaponifiable substances were obtained. The alcohols were then converted into the corresponding acetates by boiling with acetic anhydride, and the mixture of acetates was subjected to fractional distillation in a vacuum. Four fractions of about equal amount were obtained between 295° and 315°, having the saponification values 187·7, 185·0, 183·0, and 168·0 respectively. These figures do not bear out Allen's assertion that sperm oil contains alcohols of the formulæ $C_{12}H_{26}O$ and $C_{15}H_{32}O$, for the acetates of dodecatyl and pentadecyl alcohols have the saponification values 246 and 207·7 respectively. The alcohols prepared from the acetates all solidified on cooling. The saponification values show that these alcohols, or any way large percentages thereof, belong to alcohols of the unsaturated series.

Quantitative Estimation of Cholesterol.—It was found that the formation of cholesteryl acetate and cholesterol diiodide is quantitative, their production affording an easy means for the quantitative estimation of cholesterol and isocholesterol. D. B.

Estimation of Urea. By W. COLQUHOUN (*Chem. News*, 67, 123).—The author's apparatus is mounted on a stand, and consists of an inverted, stoppered burette, graduated from the stopcock to show tenths of a cubic centimetre; the other end is attached by india-rubber tubing to a tube provided with two side tubes, and having below the lower side tube an enlargement of 15 c.c. capacity, below which is a stopcock and another bulb of 6 c.c. capacity with another stopcock beneath it; the side tubes are connected, by india-rubber tubing furnished with clips, to two reservoirs, one containing water, the other hypobromite or hypochlorite. To use the apparatus, the lowest stopcock is closed and the intermediate one withdrawn, the urine is then introduced, by means of a special graduated pipette, into the lower bulb, the intermediate stopcock is replaced and turned off; the required quantity of hypobromite is now admitted into the larger bulb, and finally the rest of this bulb and the burette are filled with water. The uppermost stopcock being then closed, the analysis is completed by steadily running the hypobromite into the urine and subsequently measuring the nitrogen. The whole apparatus and materials should of course be at the temperature of the laboratory. To obviate repeated corrections for temperature, pressure, and tension of aqueous vapour, a table is furnished showing the quantity of urine which, under any indicated temperature and pressure, will evolve as many cubic centimetres of nitrogen as the urine contains grams of urea per litre. Good results have been obtained by the author.

D. A. L.

Estimation of Quinine in Cinchona Barks. By J. H. SCHMIDT (*Chem. Centr.*, 1892, ii, 946—947; from *Pharm. Centralhalle*, 33, 594—595).—20 grams of air dried, finely powdered bark is treated

for 24 hours with 10 c.c. of 10 per cent. ammonia, 20 c.c. of 90 per cent. alcohol, and 170 c.c. of ether, with repeated agitation. 100 c.c. of the liquid is then placed in a beaker, 27 c.c. of water and 3—4 c.c. of normal hydrochloric acid added, and the whole set aside for 24 hours to evaporate spontaneously. The residual liquid is then heated on the water bath to remove alcohol and ammonia, and neutralised with hydrochloric acid. If the liquid is too acid, the excess must be neutralised with cinchonine, not with ammonia or potash. With very rich *Ledgeriana* barks, 1—2 c.c. of acid may be necessary for the complete dissolution of the alkaloids. The supernatant liquid, which amounts to about 15 c.c. is exposed to the air, in order to precipitate a red colouring matter, filtered when clear, 2—3 grams of Rochelle salt added, heated for 15 minutes on the water bath, and then set aside for 24 hours. The precipitated tartrates are then collected, and washed by suction, with the smallest possible quantity of water. If all the quinine and cinchonidine are precipitated, the mother liquor will not give any turbidity when warmed with Rochelle salt. An allowance must be made of 0.0008 gram of quinine for each c.c. of mother liquor and 0.0004 gram for each c.c. of wash water. The tartrates are then dissolved in water containing hydrochloric acid, and repeatedly shaken with ether, until the latter is no longer coloured. The alkaloids are then precipitated with soda, and extracted by repeated agitation with ether; the ethereal extract being evaporated, dried at 100—110°, and weighed. With *Cinchona succiruba* and *C. officinalis*, the residue invariably contains cinchonidine, but this is not the case with rich *Ledgeriana* bark. The residue is, therefore, treated with a saturated ethereal solution of cinchonidine, which dissolves the quinine only; the ethereal extract is carefully decanted, the residue washed with a few c.c. of pure ether and again weighed, the loss of weight giving the amount of quinine. From the ethereal solution, the quinine can also be readily obtained as the pure white tartrate, and its amount estimated either by the polariscope or by de Vrij's method.

A. J. G.

Estimation of Tannin in Wine. By T. CHIAROMONTE (*Staz. Sper. Agrar.*, 20, 337—350).—Numerous experiments are described, undertaken in order to clear up some points in connection with the estimation of tannin by the permanganate method. Tannin solutions of known strength, and afterwards wines, were employed. The points specially studied were the effect of the amount of ammonia employed; whether the action of ammonia on the zinc tannate is oxidising or solvent; the effect of the amount of zinc acetate employed on the precipitation of zinc tannate, and finally the influence on the results of the mode of applying heat. It was found that ammonia plays an important part in the precipitation, but it both slightly dissolves and oxidises the zinc tannate, and on this account too much must not be used. An excess of zinc acetate was also found to cause a slight loss. Heating is necessary for complete precipitation, but it must be by means of a water bath, and should only be continued for a few minutes.

The following modification is recommended: 50 c.c. of wine (or 25 c.c. if much tannin is present) is evaporated on a water-bath to about one-third, made distinctly alkaline with ammonia, and treated with zinc acetate solution (10—15 c.c.) and 10 per cent. ammonia (2 c.c.). The whole is heated for a few minutes on a water-bath, allowed to cool, filtered quickly through a folded filter, and the precipitate washed with cold water. The zinc tannate is quickly dissolved in dilute sulphuric acid (15 c.c.); indigo-carmin solution (20 c.c.) is added, and the whole made up with water to about 400 c.c.; to this the permanganate solution is gradually added, until the colour changes from greenish to gold colour. With pure indigo, the change is instantaneous, and with practice great exactness may be obtained.

The solutions employed were of the following strengths: permanganate, 0.2 per cent.; zinc acetate, 1 per cent.; sulphuric acid, 20 per cent. (compare Martelli, *Staz. Sper. Agrar.*, **18**, 324; Vigna Abstr., 1891, 1399).
N. H. M.

The Chemico-legal Examination of Suspected Blood Stains. By H. STRUVE (*Zeit. anal. Chem.*, **32**, 174—178).—The author confirms the observation of Janeček (Abstr., 1892, 1369), that hæmin crystals can be obtained from the excrement of flies which have been fed with blood, but on treating the flies themselves with alcohol (70 per cent.) and with ammoniacal alcohol, he was unable to observe any trace of the characteristic absorption spectrum of blood.

M. J. S.

Detection of Horse Flesh in Food. By W. NIEREL (*Bied. Centr.*, 1893, 126).—The excess of glycogen present in horse flesh over that which is contained in the flesh of other animals is employed as the means whereby an admixture of horse flesh may be detected. Moreover, as glycogen gradually changes into grape sugar, it is necessary to estimate also the amount of sugar present in the food.
E. W. P.

General and Physical Chemistry.

Spectra of Aluminium, Indium, and Thallium. By H. KAYSER and C. RUNGE (*Ann. Phys. Chem.* [2], **48**, 126—149).—Continuing their researches on the line spectra of the elements (Abstr., 1891, 137 and 965), the authors have now investigated metals of the third group of the periodic system. Boron gives only two lines, of wave-lengths 2497·80 and 2496·84, and the rare earths and gallium were omitted from examination on account of the difficulty of obtaining the necessary material. The lines in the spectra of the remaining three elements, aluminium, indium, and thallium, may be arranged in two series of pairs of lines, the reciprocals of whose wave-lengths are given by the general formula $A - Bn^{-2} - Cn^{-4}$. In this formula, the values of the constants are:

	First Series.			Second Series.		
	A.	B.	C.	A.	B.	C.
Al.....	48308·2	156662	2505331	48244·5	127527	687819
In	44515·4	139308	1311032	44535·0	126766	643584
Tl	41542·7	132293	1265223	41506·4	122617	790683

These numbers give the first of the lines in each of the pairs. As there is a constant difference between the wave-lengths of lines in pairs of the same series, it is only necessary to alter the constant A to obtain the second lines of the pairs. The new values of the constant will then be:

	Al.	In.	Tl.
First Series	48420·2	46728·6	49337·6
Second Series	48356·5	46748·2	49301·3

H. C.

Ultra-red Spectra of the Alkalis. By H. KAYSER and C. RUNGE (*Ann. Phys. Chem.* [2], **48**, 150—157).—A criticism of SNOW's paper (this vol., ii, 58) in which the authors claim that impurity of the material used is the probable cause of the discrepancy between the above observers' results and their own calculations in certain cases.

H. C.

Absorption Spectra of Chromium Compounds. By W. LIA-PRAIK (*J. pr. Chem.* [2], **47**, 305—342).—The absorption spectra of the salts $M'_2Cr_2O_4$ are the same whether the salts be in solution

or as solids, but in the latter case the absorption bands are shifted towards the less refrangible end.

Chromium oxalate gives an absorption spectrum which differs from those shown by the double salts. But a solution of chromium oxalate with a small excess of oxalic acid gives the same absorption spectrum as that given by Croft's salt, $K_2Cr_24C_2O_4$, and with a large excess a spectrum identical with that of the salts $M_6Cr_26C_2O_4$, showing that a hydrogen salt corresponding with these exists in the solution.

The absorption spectra of the corresponding oxalates of iron, manganese, and cobalt are not analogous.

The corresponding *potassium chromium malonate*, $K_6Cr_26C_3H_2O_4 + 6H_2O$, was prepared, and its absorption spectrum is described. An analogous succinate could not be obtained.

The absorption spectra of solutions of chromium hydroxide in various organic acids are collated, and it is shown that in the case of the fatty acids the spectra are similar, but the bands are shifted towards the less refrangible end of the spectrum as the molecular weight increases.

The band 710—692 is characteristic of all the compounds examined, save potassium chromium cyanide, but is not absolutely identical in every case. The general absorption in the green, 650—550, is also universal.
A. G. B.

An Electrical Furnace. By H. MOISSAN and J. VIOLLE (*Compt. rend.*, 126, 549—551).—The furnace consists of a carbon receptacle in which the arc from two horizontal electrodes acts on the substance in the furnace. The receptacle is a portion of a carbon tube, the height of the segment being equal to its diameter, and it stands upon a carbon plate and is covered with a disc of the same substance. The electrodes also consist of carbon, and all the carbon parts of the apparatus are prepared from powdered gas carbon and tar, without any boric acid. The carbon cylinder and electrodes are enclosed in a block of lime, from which they are separated by a layer of air 5 mm. in thickness; the cylinder being supported on props of magnesia. The dimensions of the furnace and of the electrodes depend on the power of the current and the temperature that is desired: but there is no difficulty in obtaining a temperature of 3000°.
C. H. B.

Behaviour of Solid Colloidal Silver towards the Electric Current. By C. BARUS and E. A. SCHNEIDER (*Ann. Phys. Chem.* [2], 48, 327—337).—The previous determinations of the conductivity of colloidal silver made by the authors (*Abstr.*, 1891, 1412) not agreeing with the results obtained by Oberbeck, the experiments have been repeated, and the former conclusions have been thus in every way confirmed.
H. C.

New Method of determining the Melting Point of Inorganic Substances. By A. POTILITZIN (*J. Russ. Chem. Soc.*, 24, 1—23).—After discussing at considerable length the means which have been adopted for determining the fusing point of substances melting (a) below 300°, and (b) above 300°, the author gives the following

method for finding the temperature of fusion for substances which melt not higher than 450° , the highest temperature which a nitrogen-filled mercury thermometer can indicate. A hard glass tube, of about 5 mm. bore and 500—600 mm. long, is drawn out to capillary fineness at one end, and bent at right angles about 150 mm. from the other end. The capillary is dipped into the molten substance, the melting point of which is to be determined; so that, on cooling, the tube is closed by a solid plug of the substance 3—4 mm. long. The other end is connected with a manometer by means of which a pressure exceeding that of the atmosphere is maintained within the tube. The tube, along with the principal thermometer, and one for stem correction, is inserted into a wide test-tube, which is then immersed in a bath of fusible metal; when the melting point is reached, the plug softens and is expelled by the excess of pressure inside the tube, so that the sudden equalising of pressure in the manometer indicates the moment at which the substance melts, the thermometers being then read off. Potassium nitrate was found by this method to melt at 336.57° (mean of eight experiments ranging from 336.40° to 336.71°): by immersion of the thermometer direct into a large mass of the salt, the melting point was found to be 336.0° . J. W.

Nature of Solutions. By A. REYCHLER (*Bull. Soc. Chim.* [3], 7, 812—819).—After pointing out difficulties in the way of accepting the Arrhenius' theory of electrolytic dissociation in solutions, the author proposes to substitute for it the view that salt molecules undergo hydrolytic dissociation in dilute solution. An explanation of the mechanism of electrolysis is given based upon this view.

H. C.

Influence of Gravity on the Concentration of Solutions. By V. TURIN (*J. Russ. Chem. Soc.*, 24, 90—91).—The author has developed the following formula to express the influence of gravity on the concentration of a solution

$$hg = \frac{p_0}{\sigma_0} \cdot \log \frac{\sigma}{\sigma_0} \cdot \frac{1}{\left(\frac{\partial \sigma}{\partial \rho}\right)},$$

in which h is the depth, p_0 the osmotic pressure at the depth $h = 0$, σ_0 the concentration at h_0 , σ the concentration at h , ρ the density of the solution corresponding to the concentration σ . In J. J. Thomson's formula $\partial \sigma / \partial \rho = 1$, that is, the tacit assumption is made that the volume of solution containing 1 gram of solvent is equal to the volume of 1 gram of the pure solvent. The author suggests experimental verification by rotating a long tube, filled with solution, radially round an axis revolving at a high speed. J. W.

Electric Conductivity and Freezing Point of Aqueous Solutions of Fluorine Compounds. By R. SPERANSKY (*J. Russ. Chem. Soc.*, 24, 304—309).—All ferric salts which are electrolytically dissociated give yellow aqueous solutions; those which are hydrolytically dissociated give reddish-brown solutions. As aqueous solu-

tions of ferric fluoride are colourless, it seemed probable that neither electrolytic nor hydrolytic dissociation played any part in them, and the author has instituted experiments to ascertain if this view is correct. The electrical conductivity of the solutions is very small, so that there can be no appreciable electrolytic dissociation. The practical absence of hydrolytic dissociation is demonstrated by the fact that the solutions scarcely effect any inversion of cane sugar. Determinations of the freezing point give a molecular weight for dilute solutions nearly corresponding with the formula FeF_3 . In more concentrated solutions, there are indications of the existence of complex molecules, probably Fe_2F_6 .

Similar experiments were made with chromic fluoride and aluminium fluoride. In their case also, the molecules existing in aqueous solution are predominantly CrF_3 and AlF_3 , although there is slight electrolytic dissociation and also aggregation to Cr_2F_6 and Al_2F_6 molecules. The violet modification of chromic fluoride conducts electricity much better than the green modification. J. W.

Dissociation of Sodium Chloride in presence of Heated Surfaces of Porous Clay. By DE SANDERVAL (*Compt. rend.*, 116, 641).—When a tube of porous earthenware is heated in an atmosphere of sodium chloride vapour mixed with dry air, the interior of the tube becomes filled with chlorine, whilst only traces of this gas exist in the atmosphere outside the tube. Chemical action takes place between the sodium chloride and the silica of the tube, and there is also dissociation under the influence of heat. The evolution of chlorine ceases as soon as the pores of the tube are closed by the formation of a glaze of silicates on its external surface. The theory of these changes was explained by the author in 1886.

C. H. B.

Rate of Diffusion of Dextro- and Lævo-rotatory Tartaric acid. By L. MARCHLEWSKI (*Ber.*, 26, 983—984).—A tube about 90 cm. long, packed with six rolls of filter paper, was placed vertically, with the lower end in a 6 per cent. solution of racemic acid, and removed as soon as the top roll became wet, the experiment being then repeated several times. Neither the residual solution nor that absorbed by the filter paper showed optical activity; hence the molecules of dextro- and lævo-rotatory tartaric acid (into which the molecules of racemic acid are completely dissociated in dilute solution) must have diffused with equal rapidity.

C. F. B.

Determination of the Atomic Weight by the Method of Limit. By G. HINRICHS (*Compt. rend.*, 116, 753—756).—In atomic weight determinations, the errors increase with the amount of substance employed. To obtain the true atomic weight, a series of determinations should be made with gradually increasing amounts of material, and the atomic weight calculated not from the mean of all determinations, but from the limiting value corresponding with zero weight of substance. The author recalculates Dumas' determinations of the composition of water by this method, and obtains $\text{H} = 1$ for $\text{O} = 16$.

H. C.

General Method for the Calculation of the Atomic Weight from the Data of a Chemical Analysis. By G. HINRICHS (*Compt. rend.*, 116, 695—698).—The ordinary method of determining atomic weights is to fix one of them, say A , arbitrarily, and from this to determine the others, $B = k_1 A$; $D = k_2 B = k_1 k_2 A$; and finally, $x = k_1 k_2 \dots k_n A$. In this method all the quantities k contain unknown errors, and the constant accumulation of these errors will, in the end, prevent all chance of exactness. Since, when $O = 16$, most of the atomic weights approximate to whole or half numbers, the author proposes the following method for calculating atomic weights, as being free from the above objection. Suppose A, B, \dots, X to be the true atomic weights, and A_0, B_0, \dots, X_0 to be the whole numbers nearest to each, then

$$A = A_0 + a, B = B_0 + b, \dots, X = X_0 + x,$$

where a, b, \dots, x , are small numbers compared with A_0, B_0, \dots, X_0 . Let $\alpha, \beta, \dots, \xi$ be the coefficients corresponding to the unit of weight, then

$$A = A_0 (1 + \alpha), B = B_0 (1 + \beta), \dots, X = X_0 (1 + \xi).$$

From this the ratio $X/A = X_0/A_0 (1 + \xi - \alpha)$.

H. C.

Inorganic Chemistry.

Action of Ammonia on Hypochlorites. By J. THIELE (*Annalen*, 273, 160—163).—When a sufficiently dilute solution of sodium hypochlorite is treated with ammonia in the cold, evolution of gas does not take place, and the mixture, although still containing a considerable quantity of hypochlorite, has powerful reducing properties. A solution prepared in this way slowly reduces ammoniacal silver solutions in the cold, more quickly on warming, and precipitates cuprous oxide from solutions of copper salts; it rapidly reduces potassium permanganate to manganous oxide on heating, and at the same time it decolorises indigo solution. On evaporating such a solution to dryness, the residue is without reducing power; when, however, a solution prepared by adding chlorine water to ammonia is distilled under reduced pressure, the distillate has powerful reducing properties, but not if the solution be treated with soda before distilling.

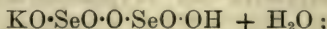
Attempts to ascertain whether the reducing properties of such solutions were due to the presence of hydroxylamine or hydrazine were unsuccessful. F. S. K.

Influence of Temperature on the Formation of Ozone. By A. BEILL (*Monatsh.*, 14, 71—80).—The author finds that the percentage volume of oxygen converted into ozone is only increased very

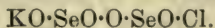
slightly by considerably lowering the temperature. For example, oxygen, dried by calcium chloride, was found to contain 5.2 per cent. of ozone when passed through the ozoniser at a temperature of 20°; whilst at temperatures of 0°, -20°, -46°, and -73°, the percentages formed were 6.8, 7.8, 9.2, and 10.4 respectively. The author gives a description of the apparatus and of the method employed, and has plotted out his results in the form of curves. G. T. M.

Selenium Compounds. By W. MUTHMANN and J. SCHÄFER (*Ber.*, 26, 1008—1016).—*Seleniobromides*.—By dissolving selenious anhydride in hydrobromic acid, adding potassium or ammonium bromide, and concentrating the solution, regular octahedral crystals of the salts K_2SeBr_6 or $(NH_4)_2SeBr_6$ are respectively obtained, isomorphous with the analogous tellurium and platinum compounds. They are orange-red in colour, but are decomposed by water into selenious acid, hydrobromic acid, and alkali bromide, yielding a colourless solution. Neither a sodium nor a silver compound could be prepared.

Chloro- (and bromo-) pyroselenites.—When an attempt is made to procure analogous chlorine compounds, colourless, monoclinic crystals of a compound $M'Cl_2 \cdot 2SeO_2 \cdot 2H_2O$ are obtained; these were prepared in the cases $M' = K, NH_4$, and Rb . When the mother liquor from the above-mentioned potassium seleniobromide is allowed to evaporate slowly, crystals of the salt $KBr \cdot 2SeO_2 \cdot 2H_2O$ are deposited; the corresponding ammonium compound was also prepared. If a solution of the potassium chlorine salt is treated with silver oxide, the solution filtered from silver chloride, and evaporated, crystals of Nilson's potassium tetraselenite, $KHSeO_3 \cdot H_2SeO_3$, are deposited. It is suggested that the substance, since it loses only two-thirds of its water at 100°, is really potassium hydrogen pyroselenite,



the original compound, from which this was derived by substituting OH for Cl, would then be potassium chloropyroselenite,



Estimation of Selenium.—This may be effected with tolerable accuracy by adding a hydrochloric acid solution of potassium iodide) with which selenious acid yields iodine, selenium, and water) and titrating the iodine with thiosulphate solution; the presence of selenium rather obscures the end-reaction with starch. C. F. B.

Hydroxylamine. By W. WISLICENUS (*Ber.*, 26, 771—774).—It has been shown by V. Meyer that hydroxylamine sulphate and sodium nitrite in concentrated aqueous solution undergo mutual decomposition at the ordinary temperature with rapid evolution of nitrous oxide; in dilute solution, the action also takes place on heating, but at lower temperatures the decomposition only proceeds slowly, and on treating the solution with silver nitrate a yellow precipitate of silver hyponitrite, $Ag_2N_2O_2$, is formed, and may be purified by dissolving it in cold dilute nitric acid and reprecipitating with ammonia. The production of hyponitrous acid may be shown as a lecture

experiment by dissolving hydroxylamine sulphate (2—3 grams) and the equivalent quantity of sodium nitrite separately in water—the total volume should not exceed 200 c.c.; the solutions are mixed and a portion tested with silver nitrate, a white precipitate of silver sulphate and silver nitrite being produced; the remainder of the solution is quickly heated to 50° on the water-bath for a few moments, the evolved gas being tested with a glowing splint of wood; on adding silver nitrate to the warm solution, a yellow precipitate of silver hyponitrite will be formed. The exact time during which the heating should be continued may be readily ascertained by a preliminary experiment.

J. B. T.

Properties of Diamonds. By H. MOISSAN (*Compt. rend.*, 116, 460—463).—The author has determined by means of a Le Chatelier thermo-electric couple the temperature at which diamonds begin to burn in oxygen. When the temperature is raised slowly, the combustion of the diamond takes place slowly and without recognisable evolution of light, its occurrence being indicated only by the action of the issuing gas on baryta solution. At 40° to 50° above the point at which this slow combustion takes place, the combustion becomes rapid, and a distinct flame is visible. The following results were obtained with eight different specimens:—Yellowish-brown carbonado burned with a flame at 690° ; black carbonado with a flame at 710 — 720° ; transparent Brazilian diamond, without a flame, at 760 — 770° ; transparent crystallised Brazilian diamond, without a flame, at 760 — 770° ; cut diamond from the Cape, without a flame, at 780 — 790° ; Brazilian bort, without a flame, at 790° , and with a flame at 840° ; Cape bort, without a flame, at 790° , and with a flame at 840° ; very hard bort, without a flame, at 800° , and with a flame at 875° . As a rule, the harder the diamond, the higher its ignition point.

When heated in hydrogen at 1200° , Cape diamonds undergo no loss in weight, although they may become somewhat lighter in colour, and lose their transparency; dry chlorine and dry hydrogen fluoride have no action at 1100 — 1200° . Sulphur vapour attacks diamonds only at 1000° ; but with carbonado, carbon bisulphide is readily produced at 900° . Sodium vapour has no action at 600° . Iron at its melting point attacks the diamond readily, and graphite separates on cooling; melted platinum also combines with it readily. Fused potassium hydrogen sulphate and the alkali sulphates have no action, and calcium sulphate is not reduced even at 1000° . Fused potassium chlorate and potassium nitrate have no action on the diamond; but Damour has shown that carbonado is attacked under these conditions.

When heated with alkali carbonates at a high temperature, the diamond is rapidly dissolved, with production of carbonic oxide. No hydrogen is, however, given off, and hence the author concludes that diamonds contain neither hydrogen nor hydrocarbons.

C. H. B.

The Ash of Diamonds. By H. MOISSAN (*Compt. rend.*, 116, 458—460).—The diamonds were treated with hydrofluoric acid, and

then with aqua regia, and were afterwards washed, dried, and burnt in oxygen. In all cases, except one, the ash was composed chiefly of ferric oxide. Bort from the Cape contained also silica, calcium, and magnesium; whilst Brazilian carbonado contained silica and calcium, but only very minute traces of magnesium.

One specimen of green, transparent bort from Brazil left a very minute quantity of ash, which contained silica, but no iron.

C. H. B.

Graphite and Graphitite. By W. LUZI (*Ber.*, 26, 890—895).—In previous papers (*Abstr.*, 1892, 406, 945), the author has shown that the varieties of carbon usually classed as graphite may be divided into two classes, according as they swell up on moistening with strong nitric acid and igniting or not. He proposes to retain the name graphite for the first class, and to term the varieties which do not show the reaction graphitite. In the present paper, it is shown that the two classes also behave in a different manner towards other reagents. Graphite from three different sources, when treated with concentrated nitric acid and potassium chlorate, yields the so-called graphitic oxide in thin, transparent, laminated crystals which, on heating, swell up very considerably, forming a loosely-aggregated mass of fine threads, termed by the author pyrographitic oxide. Graphitite from varying sources, on the other hand, gives a graphitite oxide which consists of a powder, showing no crystalline form, and on heating does not swell up, but yields pyrographitic oxide as a fine powder.

H. G. C.

Intumescent Graphite. By H. MOISSAN (*Compt. rend.*, 116, 608—611).—Luzi observed that when certain specimens of natural graphite are moistened with nitric acid and heated, they swell up and form dendritic or vermiform masses, whilst other specimens do not show this behaviour; the former he proposed to call graphites, and the latter (which include carbon from cast iron and from the electric arc) graphitites. Luzi obtained intumescent graphite from Ticonderoga, Quebec, Ceylon, Spain, Norway, and many other localities, and the author has found it in the blue earth from the Cape Diamond Fields (this vol., ii, 285).

When molten cast iron is rapidly cooled by means of water, the external layer of the ingot contains ordinary graphite, but the layers below contain the intumescent graphite as well.

In order to obtain the intumescent variety alone, platinum is melted in a carbon crucible in an electric furnace. It melts rapidly, and, after a few minutes, distils and condenses in fused drops on the colder part of the electrodes. After five minutes, the current is cut off, the metal is allowed to cool in the carbon crucible, and the platinum is dissolved by repeated treatment with aqua regia, the residue, which amounts to 1.45 per cent., being washed with water and dried.

The variety of graphite thus obtained forms hexagonal plates paler in colour than graphite from cast iron, and with parallel striæ and triangular markings in lower relief than those seen on diamonds; sp. gr. = 2.06 to 2.08. It burns in oxygen at 575°; at 400° it swells up in the same way as mercuric thiocyanate, and at a dull-red heat

intumesces abundantly. The light mass left after intumescence is graphite, and yields green graphitic oxide when treated with nitric acid and potassium chlorate, the product becoming pale yellow on a second treatment.

This variety of graphite is not attacked by potassium nitrate at its melting point, but at a higher temperature the graphite intumesces, and is afterwards destroyed somewhat rapidly, although rarely with incandescence. Fused chromic anhydride is practically without action, but at the moment of its decomposition a little carbonic anhydride is given off. On the other hand, iodic acid, when gently heated, attacks it readily, iodine and carbonic anhydride being given off. Fused sodium carbonate also attacks it rapidly, but sulphuric acid is without action, even when boiling.

Two analyses of the product obtained by means of platinum gave C, 99.02; ash, 1.10 = 100.12; and C, 98.94; ash, 1.02 = 99.96.

When the intumescence takes place, nitrogen oxides and a small quantity of carbonic anhydride are given off, but on a second treatment with the acid, only traces of the gas are evolved, and a third treatment is without any effect. It would seem, therefore, that the intumescence is due to a sudden evolution of gas, resulting most probably from the action of the nitric acid on small quantities of amorphous carbon enclosed between the lamellæ of the graphite.

C. H. B.

Preparation of Pure Rubidium Salts. By W. MUTHMANN (*Ber.*, 26, 1019—1020).—Commercial "pure" rubidium salts contain small quantities of caesium and potassium which it is difficult to detect by means of the spectroscope. To obtain a pure salt, commercial rubidium chloride (30 grams) is dissolved in very strong hydrochloric acid (250 c.c.) and antimony chloride (2.5 grams) dissolved in strong hydrochloric acid is added. The small precipitate (about 1.4 grams RbSbCl_4 and CsSbCl_4) is filtered off on an asbestos filter, the filtrate evaporated almost to dryness, the antimony still present removed with hydrogen sulphide, and the resulting mixture dissolved in strong hydrochloric acid. Rather more of a hydrochloric acid solution of stannic chloride is added than is necessary to form the stannichloride Rb_2SnCl_6 ; this substance is then precipitated, whilst potassium stannichloride, K_2SnCl_6 , remains in solution. The precipitate is allowed to settle, washed several times by decantation, collected on an asbestos filter, dissolved in water, and the tin removed with hydrogen sulphide. The rubidium chloride so obtained is pure; 0.44 gram contained 29.30 instead of 29.34 per cent. of chlorine.

C. F. B.

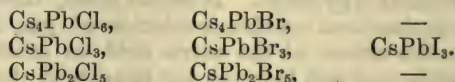
Zinc and Cadmium Fluorides. By C. POULENC (*Compt. rend.*, 116, 581—584).—Crystallised and anhydrous zinc fluoride can be obtained by (1) the action of dry hydrogen fluoride on zinc at a red heat, (2) the action of dry hydrogen fluoride on fused zinc chloride at 800—900°, (3) the action of dry hydrogen fluoride on zinc oxide or on the hydrated fluoride at a red heat. It forms slender, colourless, transparent needles, which act strongly on polarised light, and seem to belong to the monoclinic or possibly the triclinic system; sp. gr. at 15° = 4.84. It is insoluble in alcohol of 95°, and is only slightly

soluble in cold water, but the solubility in water increases with the temperature. Boiling hydrochloric, nitric, or sulphuric acid dissolves it, hydrogen reduces it at a red heat, hydrogen sulphide converts it into zinc sulphide, and hydrogen chloride converts it into zinc chloride. When heated in air, or to redness in water vapour, it is completely converted into zinc oxide, and when fused with alkali carbonates, it yields zinc oxide and an alkali fluoride.

Anhydrous cadmium fluoride is obtained in the same way, but lower temperatures are required than in the case of zinc. It forms a colourless, translucent, "crackled" product of sp. gr. 6.64. It is somewhat soluble in water, but is insoluble in alcohol of 95°, and in all other properties is strictly analogous to the zinc compound.

C. H. B.

Cæsium and Potassium Lead Haloïds. By H. L. WELLS (*Amer. J. Sci.*, 45, 121—134).—As a continuation of the investigations on double haloïds (*Abstr.*, 1892, 773; this vol., ii, 67), a study of the cæsium lead salts has been undertaken. The following salts have been established :—



These results show the existence of three types of lead double haloïds.

The method of preparation, the properties of the salts, and the analytical methods employed are fully described.

B. H. B.

Atomic Weight of Thallium. By C. LEPIERRE (*Compt. rend.*, 116, 580—581).—The starting point in these determinations was pure crystallised thallic oxide, prepared by fusing the sulphate, nitrate, or chloride with pure potassium hydroxide. The estimations made were (1) weight of thallium from thallic sulphate by electrolysis ($\text{Tl} = 203.52$ to 203.69), (2) weight of thallium in thallic oxide, after conversion into sulphate and electrolysis ($\text{Tl} = 203.53$ to 203.73), (3) weight of thallic oxide from a known weight of thallic salts ($\text{Tl} = 203.44$ to 203.79), and (4) relation between the thallium and oxygen in thallic oxide as determined by reduction in hydrogen ($\text{Tl} = 203.54$ to 203.60). The mean of eleven determinations gave $\text{Tl} = 203.62$.

C. H. B.

As neither the standard nor any details as to the methods employed are given, it is impossible to form any opinion as to the value of the results. [EDITORS.]

Purification of Mercury. By W. JÄGER (*Ann. Phys. Chem.* [2], 48, 209—212).—After distillation in a vacuum in a specially constructed apparatus in which the use of grease for the taps or of india-rubber for the connections was avoided, the mercury was converted into mercurous nitrate and deposited electrolytically from a solution of this salt. A platinum electrode served as cathode, and as anode distilled mercury was used. A current of 1 to 3 ampères was used, this giving 0.004—0.012 ampère at the cathode and 0.001—0.003

ampère at the anode per sq. cm. The absence of heavy metals in the mercury finally obtained was ascertained by careful analysis.

H. C.

Samarium. By L. DE BOISBAUDRAN (*Compt. rend.*, **116**, 611—613 and 674—677).—The head products of a fractionation of Cleve's samarium by ammonia, which contain the greater part of Z_{β} and show the electrical rays Z_{ϵ} and the reversal band Z_{ζ} , were fractionated with oxalic acid. The head of this fractionation is white and does not show the reversal band Z_{β} , but the tail is yellow and shows Z_{β} , whilst the reversal spectra of samarium and Z_{ζ} and the electrical rays Z_{ϵ} have practically the same intensity in both the head and tail. No product was obtained which, in presence of hydrochloric acid, gave Z_{ζ} distinctly stronger than the orange samarium band, whilst both bands differ little from those obtained from the original samarium under good experimental conditions. It would seem that there is a close connection between Z_{ζ} and the so-called abnormal band; both are seen with material rich in samarium and increase in intensity when the three samarium bands tend to diminish.

In yttrium sulphate containing much samarium, the abnormal band has the wave length indicated by Crookes, but in gadolinium, lanthanum, and terbium oxides containing samarium, its position varies between λ 609.1 and λ 612.9.

The line 619.6 observed in a vacuum with a mixture of lanthanum and samariferous gadolinium sulphates seems not to belong to Z_{β} , because it can be obtained with a mixture of yttria free from Z_{β} and samaria also free from Z_{β} .

The addition of hydrochloric acid to an aqueous solution of samarium chloride distinctly increases the intensity of Z_{ζ} , which becomes well defined at the more refrangible edge and nebulous towards the red, the apparent centre of the band being at λ 614.4 and the more refrangible edge at λ 611.8. Nitric acid has a similar effect on solutions of samarium nitrate, but the band is nebulous at both edges and the apparent middle of the band is at λ 615.5, the more refrangible edge being at λ 614.4. Acetic acid tends to prevent the production of the band Z_{ζ} , but this influence can to some extent be counteracted by the presence of hydrochloric acid or nitric acid.

Z_{β} and Z_{ζ} both increase in intensity in presence of excess of hydrochloric acid, but Z_{α} is much less affected. Nitric acid, on the other hand, greatly increases the intensity of Z_{ζ} but has much less effect on Z_{β} .

An aqueous solution of the chlorides of an earth rich in Z_{α} and Z_{ζ} showed Z_{α} much stronger than Z_{β} , but when the liquid was mixed with half its volume of hydrochloric acid, Z_{β} became more intense than Z_{α} . An aqueous solution of the nitrates of the same earth showed Z_{α} much stronger than Z_{β} , but on addition of nitric acid the intensity of Z_{β} increased, without, however, becoming equal to that of Z_{α} . On now adding hydrochloric acid, Z_{β} became more intense than Z_{α} . The greater the proportion of the earth in the solution of the chlorides or nitrates, the greater seemed to be the intensity of Z_{ζ} as compared with the orange band of samarium.

C. H. B.

Industrial Preparation of Alumina. By A. DITTE (*Compt. rend.*, 116, 509—510).—It is customary to treat the aluminous mineral such as bauxite with sodium hydroxide and to mix the aluminate thus obtained with a small quantity of crystallised alumina, such as is obtained by the action of carbonic anhydride on a cold solution of the aluminate. After some hours, practically the whole of the alumina has separated in an easily washed form. This reaction has already been explained by the author (this vol., ii, 278, 279) and the reasons why gelatinous aluminium hydroxide will not produce the same change have been given. The mode of formation explains the freedom of the precipitated alumina from silica, phosphoric acid, &c.

C. H. B.

Preparation of Barium Permanganate. By W. MUTHMANN (*Ber.*, 26, 1016—1018).—Potassium permanganate (100 grams) and barium nitrate (140 grams) are dissolved in water ($1\frac{1}{2}$ litres), and to the boiling solution barium hydroxide is added in portions of 20 grams until no further evolution of oxygen takes place. The whole is then warmed until the solution has become colourless, the precipitate of barium manganate (containing also some peroxide and carbonate) is collected, washed five times by decantation with 5 litres of boiling water, collected on the filter-pump, washed ten times more with boiling water, suspended in water (1 litre), and carbonic anhydride and superheated steam passed into the mixture for 10 hours. The solution is then filtered twice through an asbestos filter; it contains 65—80 grams of barium permanganate.

From this solution were obtained, by double decomposition, *permanganates of caesium, rubidium, and ammonium*, of similar appearance to the potassium salt, with which the first-named is isomorphous. The ammonium salt decomposes into manganese dioxide, water, and nitrogen when its aqueous solution is boiled; when rubbed in a mortar, it explodes, manganese dioxide and ozone being among the products.

C. F. B.

Osmium. By A. JOLY and M. VÉZES (*Compt. rend.*, 116, 577—579).—Osmium can easily be fused in the electric arc, and if a current of carbonic anhydride is passed over the metal and the temperature is raised as quickly as possible, there is practically no volatilisation. The metal should be placed in a carbon capsule, as lime is attacked and a fusible compound is formed. Superficial oxidation prevents the precise colour of the metal being determined, but it seems to be bluish-grey, and has a brilliant lustre. The fused metal does not oxidise when exposed to the air at the ordinary temperature; it has a crystalline fracture, and scratches quartz, but is scratched by topaz; sp. gr. 22.48.

Osmium is in many respects similar to ruthenium, and the two form a distinct group like platinum and palladium, or iridium and rhodium. They have almost identical atomic volumes:—

	Atomic weight,	Sp. gr.	Atomic volume,
Ru	101.4	12.06	8.40
Os	190.3	22.48	8.46

C. H. B.

Mineralogical Chemistry.

Stannite from the Black Hills, Dakota. By W. P. HEADDEN (*Amer. J. Sci.*, **45**, 105—110).—The author describes a specimen of stannite from the Peerless Mine in the Black Hills. The appearance of the mass leaves no doubt that it is what remains of an original mass now in an advanced stage of alteration. The pure stannite, free from the accompanying alteration products, gave, on analysis, the following results:—

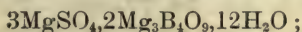
S.	Sn.	Cu.	Fe.	Zn.	Cd.	Sb.	Insoluble.
28·26	24·08	29·81	7·45	8·71	0·33	trace	1·51

These results agree with the formula heretofore accepted for stannite, except that a small portion of the zinc has been replaced by cadmium. A similar earthy mixture of stannite and its alteration products has been found in the coarsely-grained granite of the Etta Mine.
B. H. B.

Hæmatite and Martite Iron Ores in Mexico. By R. T. HILL (*Amer. J. Sci.*, **45**, 111—120).—The iron ores of Mexico have been frequently described, but no attempt has hitherto been made to define their position and origin. The author, therefore, describes in detail the geology of the Monclova ores as a typical locality of the peculiar tertiary Mexican hæmatites, and examines the distribution of similar occurrences in Mexico. The occurrence of large masses of hæmatite in rocks of cretaceous and tertiary age is of great interest, and the Mexican ores of this character, accompanied by martite, have a wide occurrence, which will probably be an important factor in the future iron supply of the world.
B. H. B.

Minerals occurring in the Westeregeln Salt-beds. By A. NAUPERT and W. WENSE (*Ber.*, **26**, 873—875).—In the nearly exhausted kainite beds at Westeregeln, lustrous, almost transparent, crystals of another mineral frequently occur, which are readily distinguished from the surrounding kainite, and consist of a new *potassium magnesium sulphate*, $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$. The same salt is also sometimes found associated with blue rock salt.

The insoluble residue left on extracting carnallite with water, which consists chiefly of anhydrite, contains also small quantities of celestine and kieserite, and a new mineral to which the name *sulphoborite* is given, as it consists of magnesium sulphoborite,



it forms distinct, apparently rhombic, crystals, which are for the most part transparent and colourless, but sometimes contain microscopic crystals of ferric oxide. It has the hardness 4, and a sp. gr. of 2·38—2·45.
H. G. C.

Anglesite associated with Boléite. By F. A. GENTH (*Amer. J. Sci.*, **45**, 32—33).—The mineral described as anglesite by Mallard and Cumenge (*Abstr.*, 1892, 123), associated with boléite from Boléo, Mexico, is found on analysis by the author to have the formula $2\text{PbSO}_4 + \text{CaSO}_4 + 2\text{H}_2\text{O}$. He concludes that these so-called anglesite crystals are pseudomorphous after a mineral of the composition $2\text{PbSO}_4, \text{CaSO}_4$, which has not yet been observed in its original condition, but only after it had taken up $2\text{H}_2\text{O}$, and changed into gypsum. This now forms a mechanical mixture with the remaining anglesite, from which it can be completely extracted by water. B. H. B.

Native Iron of Ovifak, and the Bitumen in the Crystalline Rocks of Sweden. By NORDENSKIÖLD (*Compt. rend.*, **116**, 677—678; and BERTHELOT, *ibid.*, 678).—One of the blocks of native iron collected at Ovifak, in Greenland, in 1870 is so hard that it can neither be scratched nor cut, and the author suggests that this may be due to the presence of black diamonds disseminated through the iron.

The bitumens found in the crystalline rocks of Sweden belong to two types, namely, those that yield products of destructive distillation, but leave very little ash, and those that resemble anthracite and yield practically no volatile products but leave a somewhat considerable quantity of ash.

The ash of the anthracitic bitumens contains always, in addition to silica, ferric, calcium, and magnesium oxides, &c., considerable quantities of nickel, uranium, and the cerite and gadolinite earths. This association suggests the possibility of the existence of compounds of carbonic oxide with uranium, cerium, yttrium, &c., analogous to nickel carbonyl.

Berthelot points out that in the writings of Avicenna there is mention of a metallic aërolite, which fell in the Djorjan, in Central Asia, during the 11th century, and which could neither be broken nor worked up. C. H. B.

Sulphur Compounds in Mineral Waters of Barèges. By C. NICOLAS (*J. Pharm.* [5], **27**, 128—132).—The waters of Barèges contain sulphur in various forms, such as thiosulphates and thionates, intermediate between sulphates and sulphides, and precipitable, moreover, by cadmium, but not by manganese salts. The sulphur in the various waters was estimated either by precipitation as cadmium sulphide, or by distillation with hydrochloric acid, and oxidation of the distillate with bromine, and was weighed in all cases as barium sulphate. The quantities thus obtained were usually less than those obtained by Dupasquier. JN. W.

Saline Constituents of Water from the Black Sea. By S. KOLOTOFF (*J. Russ. Chem. Soc.*, **24**, 77—89).—The following numbers were found on analysis of sea-water from different depths at a station in the Black Sea $41^\circ 50'$ N. lat, and $9^\circ 20'$ E. long. from Pulkova. The depth of water at this station is 976 Russian fathoms.

Depth.	50 fathoms.	100 fathoms.	900 fathoms.
Specific gravity 0°/4°	1·01471	1·01672	1·01746
Solids dried at 180°	1·8262	2·0726	2·1758
Na	0·5582	0·6254	0·6556
K	0·0202	0·0236	0·0298
MgO	0·1129	0·1278	0·1364
CaO	0·0354	0·0400	0·0428
Cl	1·1013	1·1365	1·1915
Br	0·0033	0·0037	0·0039
SO ₃	0·1142	0·1297	0·1351
CO ₂ in M''CO ₃	0·0062	0·0072	0·0039
CO ₂ in excess	0·0016	0·0010	0·0014
Equiv. acid to 1 equiv. base	0·9903	1·0006	0·9882

J. W.

Physiological Chemistry.

Origin of Fat from Proteïd in the Body. By E. PFLÜGER (*Pflüger's Archiv*, 51, 229—320).—In previous papers, the author has advanced the opinion that proteïd, and proteïd alone, is the source of muscular work; and that proteïd is not first transformed into fat or carbohydrate before it is available for this purpose, and that fat or carbohydrate taken as food are of no value in this respect.

Arising out of this is the wider question whether fat can ever originate from proteïd. From the detailed consideration of experiments on metabolic exchange, from the relation of the proportion of fat in milk to that in the blood, from the occurrence of fatty degenerations, and the appearance of adipocere after death, the possibility is rendered a certainty.

The greater part of the present dissertation is of a polemical nature; Voit's older experiments are given at length, and a new interpretation of the facts and statistics deduced therefrom given.

W. D. H.

Nutrition with Carbohydrate and Flesh, and with Carbohydrate alone. By E. PFLÜGER (*Pflüger's Archiv*, 52, 239—322).—This paper is a critical account of the older experiments of Pettenkofer and Voit on the subject. The conclusions drawn are that in many cases the decomposition of proteïd will not account for the newly-formed fat, if only starch or starch and flesh are given in the food. Body fat is only formed if a nutritive excess of carbohydrates are present. If this is not the case, the body is overloaded with carbohydrate, not fat. Fat does not appear with great excess of proteïd food if carbohydrate is not given at the same time. After feeding on flesh and starch, or an ordinary mixed diet, the amount of

newly-formed fat does not depend on the quantity of proteid which undergoes metabolism, but on the excess of carbohydrate. By feeding on carbohydrate alone, fat is seldom formed. W. D. H.

Amount of Albumin required for the Human Body. By L. BREISACHER (*Bied. Centr.*, 22, 203—204; from *Deut. med. Wochenschr.*, 1891, No. 48).—The experiments described by the author were made on himself. He weighed 52 kilos., was rather free from fat, and not very muscular. For 33 days the food, consisting of meat, rice, potato, bread, eggs, and milk, &c., contained: albumin (68 grams), carbohydrates (494 grams), and fat (60 grams) per diem; his weight remained constant. During the successive three periods of 10 days, the daily amounts of nitrogen in the urine were 8·6, 7·7, and 8·4 grams respectively, so that of the 68 grams of albumin consumed only 52 grams was deposited in the body. The results indicate that for men of average weight (70 kilos.) 87—88 grams of albumin is sufficient; provided, of course, that non-nitrogenous food is consumed in sufficient quantity. N. H. M.

Alcohol as a Substitute for Albumin under various Conditions of Feeding. By C. v. NORDEN (*Bied. Centr.*, 22, 204; from *Berl. klin. Wochenschr.*, 1891, No. 23).—Healthy men, after being brought into a condition of nitrogen equilibrium with albumin, fat, and carbohydrates, had certain quantities of alcohol given to them as a substitute for corresponding amounts of fat or carbohydrate. If the albumin-saving power of alcohol is the same as that of carbohydrate and fat, the nitrogen equilibrium should be maintained. In the first experiment, with very nitrogenous food, 65 grams of alcohol so diminished the nitrogen of the urine, that in the first two days 0·7 and 0·9 gram of nitrogen was deposited; on the third, however, and on the fourth day (without alcohol), there was a loss of 1 gram of nitrogen each day. In a second experiment, in which 25—70 grams of alcohol was given for four days, there was a loss of nitrogen of 0·2, 0·8, 1·0, and 1·8 gram, whilst in the next two days (without alcohol) 1·0 gram was lost each day. In the third experiment, a man fed with albumin (50 grams), fat (125 grams), carbohydrates (480 grams), and alcohol (65 grams), lost for eight days an average of 0·3 gram of nitrogen; with a further 65 grams of alcohol and correspondingly less fat, there was, in the one day of the experiment, a deposition of 2·3 grams of nitrogen.

It is concluded that, with richly nitrogenous food, the Calories of alcohol will be well utilised, but not otherwise. N. H. M.

Feeding Experiments with Sunflower Cake, on Cows. By KLEIN (*Bied. Centr.*, 22, 175—177; from *D. Landwirth*, 1892, 462 and 468).—Four lots of four Dutch cows were fed as follows:—Maize and potato-distillery liquor (17 litres), dried brewers' grains (1·5 kilos.), linseed cake (0·5 kilo.), meadow hay (2·5 kilos.), chaff (1·5 kilos.), scalded wheat and summer straw (5·0 kilos.), summer straw (2—2·5 kilos.). The total food contained dry matter (12·6 kilos.), digestible albumin, fat, and carbohydrates, 0·96, 0·29, and 5·67 kilos.

respectively. The nutritive ratio was, therefore, 1 : 6.5. For the first week of the experiment this feeding was continued, in the second week the additional food was given in increasing amounts, and in the third and fourth weeks the full amount was given; in the fifth week the amount of additional food was decreased, and in the last two weeks the cows had only the original food. The first group had no additional food, group 2 had 2.05 kilos., group 3, 1.0 kilo. of sunflower meal; group 4 had 4.05 kilos. of linseed and 0.5 kilo. of sunflower cake meal per head daily. With the full amount of extra food, the nutritive ratio was 1 : 5.8 for group 2, 1 : 5.3 for group 3, and 1 : 5.4 for group 4. Having regard to the natural decrease in amount of milk with the advance of the period of lactation, it is calculated that in the third and fourth weeks, there was a daily increase of 0.8 litre per head in group 2, 0.84 litre in group 3, and nearly 0.6 litre in group 4, as a result of the extra food. So that the larger amount of sunflower cake did not give any considerably increased yield over the less. On the whole, sunflower cake seems to be superior to linseed cake in increasing yield of milk. The amount of fat showed great variations, attributed rather to varying composition of the food (especially the distillery liquor) than to the extra food. The unfavourable results are thought to be due to the fact that the original feeding was sufficient without that added for the purpose of experiment.

N. H. M.

Influence of Caffeine and Coffee Distillate on Metabolism.

By W. HEERLEIN (*Pflüger's Archiv*, 52, 165—185).—The present experiments relate chiefly to gaseous metabolism, a modification of the Regnault-Reiset apparatus being used. The general conclusion drawn is that coffee is neither in itself nutritive, nor does it act as a "sparing" food. It, however, stimulates metabolism, probably by its action on the nervous system. This is especially marked after injections of caffeine, the amount of oxygen used being always increased. The distillate of coffee smells like coffee; its chief constituent is caffeine, $C_8H_{10}O_2$ (probably methylsaligenin, O. Bernheimer). It has practically no effect on gaseous interchanges. Rabbits were used chiefly in these experiments.

W. D. H.

Influence of Ligature of the Bile Duct on Metabolism.

By N. P. KRAWKOW (*Chem. Centr.*, 1893, i, 262—263; from *Wratsch*, 1891, No. 29).—Dogs were dieted to constant weight, and then subjected to inanition. They died after a loss of 35—40 per cent. of their body weight, and this occurred more rapidly if the bile duct had been previously ligatured.

W. D. H.

Hydrolytic Ferments. By H. HILDEBRANDT (*Virchow's Archiv*, 131, 5—39).—When hydrolytic ferments are introduced into the animal organism, they cause fever. The present experiments, performed with chymosin (rennin), invertin, and emulsin, show further that, locally, they excite positive chemiotaxis. With regard to the fate of hydrolytic ferments in the organism, the experiments were made with emulsin and myrosin, these ferments being foreign to the

animal body. After large doses, administered by subcutaneous injection in rabbits, none was ever found in the urine; but up to six hours after the injection, the administration of amygdalin produced poisoning by hydrocyanic acid. Beyond this time, this did not occur. The question arises, Does the action between ferment and glucoside take place in the blood or in the tissues? It may possibly occur in the blood, as 10 minutes after subcutaneous injection, intravascular injection of amygdalin causes death from hydrocyanic acid poisoning; the same occurs after simultaneously injecting the two substances into different vessels. But as it may also occur when no ferment is discoverable in the blood later on, it probably may occur in the tissues. At the *post-mortem*, ferment is found in the liver in great abundance, and to a less extent in the spleen and pancreas. It is absent from muscle, bile, gastric and intestinal juices, and intestinal walls. It may be found in the liver cells 17 hours after injection, a period when administration of amygdalin produces no result. The ferment is contained in the liver either as an inactive modification or else so that it cannot leave the cells, or it may be that the amygdalin cannot then get into the cells. One has, therefore, to investigate the fate of the injected amygdalin. It appears to be excreted by the kidneys in part. The function of the liver in arresting various poisons is well known. Extracts of the living liver hinder the interaction of emulsin and amygdalin; similar aqueous extracts of dead liver have no such effect. The living liver has a similar hindering action on the action of rennin. The living blood acts similarly, and the change is probably that the ferment is converted into an inactive modification. The injected ferment seems to cause degenerative processes to occur in the liver cells. It also produces other physiological actions, such as stopping the heart in diastole and muscular paralysis.

Aqueous extracts of the fruit of *Syzygium jambolanum* hinder saccharifying actions. Diabetes may be artificially produced by puncture of the medulla, or by phloridzin; or by stimulation of the depressor nerve. In experiments performed under the two latter conditions, extracts of *Syzygium* appeared to have a distinct action in lessening saccharification in the organism. In such experiments, it is necessary that the extracts should be themselves free from sugar, and neutralised, as their original acidity, diminishing the alkalinity of the blood, tends to produce diabetic phenomena.

In conclusion, experiments are recorded which show that, by the administration of successive very small doses of ferments, a certain amount of immunity to larger doses is brought about.

W. D. H.

Synovia and Mucin. By E. SALKOWSKI (*Virchow's Archiv*, 131, 304—326).—The chief point of interest in connection with synovia is the nature of the mucinoid substance contained therein.

Mucin from the submaxillary gland was found to contain no phosphorus, or only traces, and readily yielded a reducing substance on treatment with dilute mineral acid. The same is true for paralbumin. Nucleohiston from the thymus contains 2·8 per cent. of phosphorus (Lilienfeld gives 2·4), and yields no reducing substance. Casein contains 0·89 per cent. of phosphorus, and yields no reducing

substance. Vitellin from egg yolk contains 0.95 per cent. of phosphorus, and yields no reducing substance. Mucin from urine contains 1.8 per cent. of phosphorus, and yields no reducing substance; it is, in fact, nucleo-albumin. The synovial mucin is neither true mucin nor nucleo-albumin. It contains no phosphorus, but yields no reducing substance.

W. D. H.

Method of estimating the Volume of the Corpuscles of the Blood. By M. BLEIBTREU and L. BLEIBTREU (*Pflüger's Archiv*, 51, 151—228).—By estimating the nitrogen by Kjeldahl's method in mixtures of blood and salt solutions, and in the serum of the same blood, data are obtained for calculating the amount of nitrogen in the corpuscles, and thence the proportion of corpuscles in the blood. In the present experiments, horse's blood was used. Mixture with magnesium sulphate solutions gave results in which the proportion of corpuscles is obviously too low. Trustworthy results were obtained by mixing the blood with known volumes of physiological salt solution, which leaves the corpuscles intact. Further, in most experiments, defibrinated blood was used; removal of the fibrin only makes a difference in the percentage of total proteids in the first decimal place.

The equation obtained is as follows:—

$$(e_1 - e_2)x = \frac{s_2}{b_2}e_2 - \frac{s_1}{b_1}e_1.$$

b_1 and b_2 are the volumes of blood in two mixtures; x is the fraction by which b must be multiplied in order to obtain the volume of liquid in it; s_1 and s_2 are the volumes of salt solution; e_1 and e_2 are the amounts of proteids in the two mixtures. The volume of the corpuscles = $1 - x$.

A simpler method consists in taking the specific gravity of the mixtures, and very nearly as good results are obtained: the formula is—

$$x = \frac{s}{b} \times \frac{S - K}{S_0 - S}.$$

Here s = volume of saline solution,

b = volume of blood,

K = sp. gr. of saline solution,

S_0 = „ the serum,

S = „ the mixture.

The matter may be still further simplified by the fact that in the horse the percentage of proteid in the corpuscles was found to be an almost constant factor (46.85 per cent.), and the corpuscles of almost constant specific gravity; so that in this animal, at least, the formula may be briefly put—

$$V = 2.55 (E - e).$$

Here V = volume of the corpuscles,

E = proteid in the blood,

e = „ serum.

A rough average of the results obtained shows that the serum contains 7 to 8 per cent. of proteïd; the whole blood 18 to 22.

The volume of the corpuscles per cent. in 10 experiments gave 28·78, 38·8, 26·32, 38·45, 33·04, 39·15, 40·95, 26·14, 37·02, 34·11.

W. D. H.

Volume of Blood Corpuscles. By O. LANGE (*Pflüger's Archiv*, 52, 427—455).—A similar investigation to the preceding, carried out with the blood of the ox and pig. With the blood of the ox, five observations gave 40·05, 35·39, 26·22, 27·37, and 36·95 per cent. of corpuscles per volume. These numbers were obtained by nitrogen analyses. With the blood of the pig, all three methods were employed. By nitrogen analysis, five experiments gave the numbers 30·11, 41·61, 34·38, 41·24, and 43·41. The other methods gave almost the same numbers. The shortened formula for pig's blood is $V = (E - e) 2·71$.

W. D. H.

The Volume and Amount of Proteïd in single Red Blood Corpuscles. By H. WENDELSTADT and L. BLEIBTREU (*Pflüger's Archiv*, 52, 323—356).—Having obtained a method of estimating the proportion of corpuscles to fluid per volume in blood (see preceding abstracts), it is a simple extension to combine this with hæmocytometric observations, and thus obtain the volume and amount of proteïd in single red blood corpuscles.

This was done in horse's and pig's blood.

The mean of six observations on horse's and five on pig's blood gave the following results:—

	Horse.	Pig.
Volume of a single red corpuscle ..	0·00000003858 c.c.	0·00000004350 c.c.
Amount of proteïd therein	0·000000018023 mgm.	0·00000001928 mgm.

W. D. H.

Influence of Acids and Alkalis on Defibrinated Blood. By H. J. HAMBURGER (*Chem. Centr.*, 1893, i, 260—261; from *Du Bois Reymond's Archiv*, 1892, 513—544).—Carbonic anhydride alters the permeability of the red corpuscles, and thus plays an important part in metabolic processes, as in venous blood an exchange between their constituents and the surrounding fluid takes place. This action is not specific to carbonic anhydride, but other acids (hydrochloric and sulphuric) act similarly. The experiments were made with defibrinated blood, but it seems probable that the same is true for the circulating blood. By treatment with acids, the corpuscles yield their proteïd constituents more readily to the serum, and take up chlorides and phosphates from it. Alkali in equivalent quantities produces the opposite effect, and neutralises the action of acid. The susceptibility of the corpuscles to this action is very great, being produced by 0·00775 per cent. of potassium hydroxide and 0·0025 per cent. of hydrochloric acid.

W. D. H.

Diastatic Action of the Serum of Blood and Lymph. By M. BIAL (*Pflüger's Archiv*, 52, 137—156).—A diastatic ferment is present in the serum of blood and of lymph. It is not present in the red corpuscles. It differs from that in saliva, pancreatic juice, and germinating seeds in changing starch into dextrose, not into maltose. The quantity of dextrose obtained is the same, or nearly the same, as that obtained by treating the starch with hydrochloric acid. By sub-maximal saccharification, dextrin is formed as well. Maltose and achroodextrin are also acted on by this ferment. In the presence of glycerol, starch and achroodextrin were only incompletely converted into dextrose, maltose hardly at all. W. D. H.

Diastatic Ferment in Lymph. By F. RÖHMANN (*Pflüger's Archiv*, 157—164).—In view of the preceding investigation, it became important to discover whether this diastatic ferment exists in the circulating blood and lymph. Injection of starch or glycogen into the circulation and subsequent examination of the urine has led to contradictory results. Injection into a ligatured portion of a vein has the objection that degenerative and coagulative changes may set in, and the presence of sugar in a few minutes is not an absolute proof that living blood contains the ferment. In the present research, glycogen was injected into the lymph, and the lymph from the thoracic duct allowed to flow directly into alcohol. The percentage of sugar in the lymph always rises. Injection of physiological saline solution, the solvent used, does not produce this result.

The diastatic ferment thus proved to be present in lymph can only originate from the blood or the tissues. If the latter is the case, the ferment will pass into the blood from the lymph; a part will pass into the urine; a part remaining in the blood will produce there a saccharifying action. If, on the other hand, the ferment passes into the lymph from the blood, the experiments prove that it is contained in the plasma of the circulating blood. In either case, the dictum of Schiff that "the appearance of a diastatic ferment is the first symptom of the death of the blood" is incorrect. W. D. H.

Glycogen. By S. FRÄNCKEL (*Pflüger's Archiv*, 52, 125—126).—See this vol., i, 386.

Occurrence of Glycogen in Blood. By G. SALOMON (*Chem. Centr.*, 1893, i, 54—55; from *Centr. physiol.*, 6, 512—513).—With reference to Huppert's statement that he had discovered glycogen in blood and pus (this vol., ii, 176), the author calls attention to the fact that he had observed the occurrence of glycogen in blood and other animal liquids and effusions as far back as 1877. A. J. G.

Carbamic acid in the Urine after Ingestion of Calcium Hydroxide. By J. J. ABEL and A. MUIRHEAD (*Chem. Centr.*, 1893, i, 261—262; from *Archiv exp. Path. Pharm.*, 31, 15—29).—Dogs fed on meat free from bone have an acid urine. If from 8 to 10 grams of calcium hydroxide is added to the daily diet, their health remains unimpaired, but the urine is strongly alkaline and ammoniacal.

20 c.c. of such urine yielded 0.00336 gram of ammonia in five days; in another experiment 40 c.c. yielded 0.0074 gram of ammonia in nine days. A deposit of triple phosphate forms in the urine. On the return of the animals to flesh diet, this continues, but the yield of ammonia is not so great. Carbonic anhydride is also given off, and on boiling the urine there is a deposit of calcium carbonate. This is explained on the hypothesis that the urine contains calcium carbamate, which is readily decomposed into calcium carbonate, carbonic anhydride, and ammonia, and confirmed by the separation of calcium carbamate from the urine by Dreehsel's method (*Chem. Centr.*, 1891, ii, 713). Experiments on human beings led to the same results.

W. D. H.

Exudations and Transudations. By A. BERNHEIM (*Virchow's Archiv*, 131, 274—303).—The analysis of a large number of dropsical fluids is recorded; the sp. gr. and percentage of proteïd being specially noted. An approximation to the percentage of proteïd (E) can be obtained from the sp. gr. (S) by the following formula, $E = \frac{2}{3}(S - 1000) - 2.8$. In the case of exudations (inflammatory fluids), the result is not so correct as with transudations (pressure dropsies).

Mere chemical analysis, although valuable as part of a chain of evidence, is not by itself sufficient for a correct diagnosis of the variety or cause of the dropsy under investigation.

W. D. H.

Calculus in Muscle. By A. GASCARD (*J. Pharm.* [5], 27, 256—258).—The calculus was found in a fibromuscular sac adhering to the bronchi at the bifurcation of a woman's trachea. It weighed 5.34 grams, and had the following percentage composition:—

Water (after soaking in alcohol).....	1.7
Calcium phosphate.....	68.0
Calcium carbonate.....	14.2
Organic matter.....	14.7
Magnesia.....	trace

JN. W.

Physiological Action of Cocaine. By B. DANILEWSKY (*Pflüger's Archiv*, 51, 446—454).—In the numerous researches on this subject, attention has been specially directed to the action of cocaine on sensory nerves. It has, however, also an action in paralysing motor nerves. Langlois and Richet state that the toxic action of cocaine is proportional to the development of the cerebral system.

In the present research, observations were made on various aquatic animals belonging to the groups of the cœlenterata, echinodermata, worms, arthropoda, and mollusca. A small quantity of cocaine was added to the water, the concentration of the mixture varying from 1 to 1000—3000.

The general result may be summed up by saying that cocaine is a protoplasmic poison; it is an anæsthetic to all kinds of animals; and that its action has no relation to the development of the nervous system, still less of a central nervous mechanism.

W. D. H.

Resistance of Goats to the Action of Morphine. By L. GUINARD (*Compt. rend.*, 116, 520—522).—Morphine has no recognisable narcotic influence on goats, and when large doses are administered, death arises chiefly from disturbance of the respiratory functions. The general resistance of goats to the action of the alkaloid is very remarkable. A young goat weighing 30 kilos. showed little effect beyond a slightly increased cerebral excitability after two doses of 8.0 and 8.5 grams of morphine hydrochloride respectively administered after an interval of $2\frac{1}{2}$ hours by intravenous injection. Two days afterwards, 19.5 grams of the salt, or 0.45 gram per kilo. was administered in the same way at one injection, but after 9 hours the animal seemed to have completely recovered.

The quantity of morphine required to produce death varies considerably with the age and the health of the animal, but is not less than 0.25 to 0.30 gram per kilo. of body weight, or about 1000 times the quantity that suffices to produce narcotism in man when administered in the same way.

C. H. B.

Sulphuric acid Poisoning. By E. FRÄNKEL and F. REICHE (*Virchow's Archiv*, 131, 130—146).—A number of cases of sulphuric acid poisoning are recorded, and references to others given. The chief stress is laid on the kidney affection produced; this is a destruction of the renal epithelium. The glomeruli, vessels, and connective tissue are intact. Albuminuria is not a constant symptom.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Production of Hydrogen Sulphide and Methyl Mercaptan by a Bacterium in Urine. By J. P. KARPLUS (*Virchow's Archiv*, 131, 210—222).—The urine of a patient with pneumonia and intermittent albuminuria was clear when passed, but in a few hours became cloudy from a bacterial growth, and hydrogen sulphide and methyl mercaptan were given off. This had no relation to the presence or absence of albumin. The bacterium was a short rod, and details regarding its culture and staining properties are given. It does not produce these volatile products when grown in other albuminous fluids. It therefore acts on certain other sulphur-containing constituents of the urine. With sulphates, phenyl potassium sulphate, urinary indican, and thiocyanates, it produces no evolution of hydrogen sulphide; but with thiosulphates there is constantly an evolution of the gas. These salts, however, do not occur to any appreciable extent in normal urine. It must, therefore, be that the source of the gas is those sulphur-containing organic substances to which Salkowski has given the name of "neutral sulphur." This was confirmed by estimating this neutral sulphur before and after the action of the micro-organism.

W. D. H.

Fixation of Free Nitrogen by Plants. By T. SCHLÖESING, Jun., and E. LAURENT (*Ann. Inst. Pasteur*, 6, 824—840; compare Abstr., 1892, 1021).—Two new series of experiments are now described; the first was made with higher plants, the second with lower plants. Both were conducted in the apparatus already described (*loc. cit.*). As regards the first series, a subsoil was employed with which a small amount of a mixture of good soils was mixed for the introduction of micro-organisms. After sowing the seeds, the surface of the soil was covered with dry sand to prevent the production of lower plants. Unlike the earlier experiments, considerable amounts of nitrate were added to the soil.

In experiments 1 to 4, 2 kilos. of soil (containing 0.008727 per cent. nitrogen) was employed, in 5, 3 kilos. The amount of ignited sand was 100—200 grams. The experiments were:—(1) check, (2) oats, (3) colza, (4) grasses (*Dactylis*, *Phleum pratense*, *Holcus lanatus*, *Avena elatior* and *fatua*), and (5) potatoes. The direct method was employed only with 1 and 2, and the results were as follows:—Nitrogen employed, 759.3 and 4585.3 c.c.; loss, 0.9 c.c. and 3.0 c.c. The indirect method gave the following results:—Loss or gain: check, -0.7; oats, -2.7; colza, +0.9; grasses, +0.1; and potatoes, -6.5 milligrams of nitrogen. Under the conditions of the experiments, there was, therefore, no fixation of nitrogen.

The experiments with lower vegetation were conducted in the same apparatus, except that instead of the large cylinders, flasks were employed, which were rather less than half filled with soil (600 grams). In experiments 1 and 2, the same soil was employed as in those just described, 100 c.c. of a nutritive solution (without nitrate) was added, and after the introduction of the soil into the flask, 5 c.c. of potassium nitrate solution containing 10 milligrams of nitrogen, and 5 c.c. of soil extract were added. The surface of the soil became covered with algæ, consisting mainly of *Nostoc punctiforme* and *Nostoc minutum*, with some colonies of *Cylindrospermum majus*. There was a considerable fixation of nitrogen (see table), corresponding, in fact, with 60 kilos. per hectare. The amount of organic substance produced was (1) 1.476 and (2) 1.148 gram, and it contained 4.7 and 4.2 per cent. of nitrogen. In experiments 3 and 4, 600 grams of quartz sand, 125 c.c. of nutritive solution, and 5 c.c. of soil extract were employed; no nitrate was given. In 3, a nearly pure cultivation of *Nostoc punctiforme* was produced, in 4, a less pure cultivation of *Nostoc* with colourless masses enclosing bacteria; a colony of *Phormidium papyraceum* and some *Nostoc minutum* were found. Here again, there was considerable fixation. The organic matter found amounted to 0.827 and 0.543 gram with 4.0 and 5.5 per cent. of nitrogen. Experiments 5 to 8 were made with 600 grams of the soil with the same nutritive solution as before, and nitrate solution containing 14 milligrams of nitrogen. No soil extract was given. No 5. Tufts of *Brachythecium rutabulum* (0.114 gram) and of *Barbula muralis* (0.172 gram) were planted, samples being kept for nitrogen determination. No 6. A very small amount of green matter was suspended in water and the water added drop by drop. The resulting growth consisted of *Microcoleus vaginatus* with very small amounts of other *Oscillatoria* (*Lynghya oscilla-*

toria) and chlorosperms (*Tetraspora*, *Protococcus*, *Stichococcus*, *Alothrrix*). Nos. 7 and 8. Check experiments; nothing sown. In 8, the surface of the soil was covered with ignited sand. Two spots of green (*Phormidium autumnale* and *Nostoc punctiforme*) were formed on the surface of the soil in No. 7, whilst in No. 8 (which was covered with ignited sand, but too thinly), a spot of *Phormidium* appeared. Taking, these four experiments together, there was no appreciable fixation of nitrogen. Two more experiments (9 and 10) were made with a moss (*Homalothecium sericeum*) taken from a roof. In 9, the entire moss was employed; in 10, the brown portions only. They were introduced into flasks containing 600 grams of quartz sand with nutritive solution and nitrate. In three weeks, the green portions absorbed about 500 c.c. of carbonic anhydride, but there was no appreciable nitrogen fixation. The following table give the nitrogen results of the whole series.

Nitrogen (milligrams).

Direct method.		Indirect method.				
Initial.	Fixed.	Initial total.*	Final in soil.			Gain or loss.
			Surface.	Interior.	Total.	
c.c.	mgm.					
1. 982·9	65·0	73·5	78·3	57·8	136·1	+ 62·6
2. 847·1	37·1	73·5	57·1	57·7	114·8	+ 41·3
3. 1047·0	36·8	1·0	33·2	3·0	36·2	+ 35·2
4. —	—	1·0	30·4	3·6	34·0	+ 33·0
5. 1069·5	0·1	68·4	17·0	51·0	68·0	— 0·4
6. 784·8	—0·4	66·4	17·7	48·8	66·5	+ 0·1
7. 740·3	0·6	66·4	—	—	67·5	+ 1·1
8. 580·1	1·8	—	—	—	—	—
9. 1054·1	0·7	—	—	—	—	—
10. 965·7	0·8	—	—	—	—	—

Certain algæ which occur commonly on the surface of soils have therefore, the power of fixing free nitrogen; but, inasmuch as the cultivations of algæ experimented with were not absolutely pure, it cannot be said that certain algæ alone have the power of fixation. It is possible that the algæ effect fixation in symbiosis with bacteria.

N. H. M.

Occurrence of Trehalose in Fungi. By É. BOURQUELOT (*J. Pharm.* [5], 27, 113—120).—As previously established (Abstr., 1891, 103; 1892, 519 and 545), the trehalose is probably formed in the vegetative parts of the fungi, and disappears at maturity. In order to ascertain the period at which it is formed, various fungi

* In soil, 52·4 milligrams (Nos. 1 and 2, 5, 6, and 7); as nitrate, 10 milligrams (Nos. 1 and 2), 14 milligrams (Nos. 5, 6, and 7).

were examined at different stages of their growth. *Sclerotinia tuberosa* (Hedw.) gathered in winter contained no trehalose and 0.43 per cent. of mannitol, but at maturity 0.26 per cent. of trehalose and 0.8 per cent. of mannitol, whilst the sporophores then contained only traces of trehalose and 0.79 per cent. of mannitol. The trehalose is formed, therefore, just before fructification. In *Phallus impudicus* (Linn.), the same phenomena were observed. Glucose (0.98 per cent.) was also present; it was slightly reduced in amount (0.77 per cent.) on fructification. In specimens of *Sterigmatocystis nigra* (V. Tiegh.) artificially cultivated, the same phenomena occurred, the trehalose appearing only at fructification, none being formed beforehand or afterwards.

JN. W.

Drainage Water from Arable Soils. By P. P. DEHÉRAIN (*Ann. Agron.*, 19, 65—89).—The Rothamsted experiments have made known the relation between the nitrogen supplied as manure, that recovered in the crop, and that lost in the drainage water, in the case of wheat. But with regard to other crops there is little information. The pot experiments of the author on this subject (Abstr., 1891, 795) are open to the drawback that it is impossible to succeed with some cultures—for example, wheat, sugar-beet, and maize—in pots to the same extent as in the open ground. To remedy this, the author has had 20 water-tight cases made and sunk in the ground, access being made to one side by an excavated path, in order to collect the samples of drainage water which flow from tubes inserted in the sides at the bottom of the cases. Each case is 2 m. square (4 sq. m. surface) by 1 m. in depth, and thus holds 4 cub. m. or about 5 tonnes of soil. They were filled with subsoil and soil as it existed on the spot, and all the cultures succeeded quite as well as in open ground. The results obtained in 1892 are discussed at length. In the annexed table, the results are calculated per hectare.

The season was hot and dry, the rainfall being badly distributed. The drain tubes of the four cases under bare fallow ran on six occasions, namely, July 21, August 31, October 11, 25, November 2, 12. Those of the cases under crop ran only three times, namely, July 21, November 2 and 12. Whenever water was collected, it was measured, and 500 c.c. taken for determination of the nitric nitrogen by Schloesing's method. The loss of nitrates from the bare fallows was considerable in spite of the small rainfall; nitrification in the soil was so active in relation to the rainfall that as much nitrate was lost from the unmanured bare fallow No. 1 as from those manured, Nos. 12, 13, 14. In all cases, the nitrate lost is more or less proportional to the water running through, the richness of the water in nitrates not varying to the extent one would suppose. The crop allowing most loss of nitrate is wheat followed by autumn fallow, and next the beet grown for seed. The sowing of vetches after wheat very strikingly diminishes the autumnal loss of nitrate. Forage maize, potatoes, and sugar-beet allow little loss of nitrate, and the amount recovered in the crop is large. It was remarkable that sugar-beet in these cases succeeded much better than that in the open field plots, the germination in the latter case being affected

Case.	Culture.	Manure per hectare.	Crop per hectare.	Drainage water in mm. of height.	Nitrogen in crop, kilos. per hectare.	N as nitrate in drainage water, kilos. per hectare.	N in drainage water per cent. of N in crop.
1.	Bare fallow	None	—	89.0	—	140.6	—
2.	Rye-grass	None	6000 kilos.	27.7	77.5	19.2	23.5
3.	Sugar-beet	30,000 kilos. f.y.m.	38,250 kilos. roots.	14.0	120 in leaves and roots	4.4	3.7
4.	"	30,000 kilos. f.y.m. and 250 kilos. nitrate soda	38,250 "	8.0	120	3.2	2.6
5.	"	625 kilos. nitrate and 200 kilos. superphosphate	38,250 "	13.7	120	13.0	10.8
6.	Wheat (squarehead)	15,000 kilos. f.y.m.	{ Grain, 15.75 metric quintals Straw, 37.50 metric quintals	{ 39.7	{ 51.7 grain and straw	{ 54.6	{ 105.5
7.	{ Wheat followed by autumn vetches	15,000 kilos. f.y.m. and 200 kilos. nitrate	{ Grain, 17.00 metric quintals Straw, 40.00 metric quintals	{ 16.8	{ 55.5	{ 17.0	{ 30.7
8.	{ Wheat followed by autumn vetches	500 kilos. nitrate and 200 kilos. superphosphate	{ Grain, 19.25 metric quintals Straw, 37.50 metric quintals	{ 18.8	{ 59.0	{ 17.9	{ 30.3
9.	Potatoes, Richter's "Imperator"	30,000 kilos. f.y.m.	Tubers, 37,500 kilos.	27.6	162.5	18.2	11.38
10.	"	30,000 " f.y.m. and 250 kilos. nitrate	" 36,500 "	28.7	153.5	16.6	11.03
11.	"	625 kilos. nitrate and 200 kilos. superphosphate	" 36,250 "	29.3	157.5	19.7	12.8

Case.	Culture.	Manure per hectare.	Crop per hectare.	Drainage water in mm. of height.	Nitrogen in crop, kilos. per hectare.	N as nitrate in drainage water, kilos. per hectare.	N in drainage water, per cent. of N in crop.
12.	Bare fallow	30,000 kilos. f.y.m.....	—	97·7	—	121·2	—
13.	"	30,000 kilos. f.y.m. and 250 kilos. nitrate	—	102·2	—	156·5	—
14.	"	625 kilos. nitrate and 200 kilos. superphos- phate	—	99·2	—	144·8	—
15.	Maize (forage)	30,000 kilos. f.y.m.....	Cut green, 77,500 kilos.	16·2	190·0	14·5	7·7
16.	Clover	No manure	Hay, 2750 kilos. { Grain, 24·0 metric quintals Straw, 27·5 metric quintals	29·7	55·0	25·4	46·1
17.	Oats and clover	No manure	Seed, 2134 kilos. " 2513 "	21·7	56·0	31·1	55·6
18.	Beet for seed	30,000 kilos. f.y.m.....	44·2	Not de- termined	44·8	{	—
19.	"	30,000 " f.y.m. and 250 kilos. nitrate	" 2513 "	50·1	46·9		—
20.	"	625 kilos. nitrate and 200 kilos. superphos- phate	" 3214 "	42·8	53·3		—

by the drought. The soil of the plots was found to contain 4 and 7 per cent. moisture, that of the cases 10 and 11 per cent.

J. M. H. M.

Influence on Vegetation of the Pressure of Carbonic Anhydride in the Air of Soils. By S. JENTYS (*Ann. Agron.*, 18, 594—597; from *Bull. Acad. Sci. Cracovie*, July, 1892).—The interstitial air of soils is well known to be much richer in carbonic anhydride than the atmosphere—in soil recently manured, the proportion may reach 10 per cent. The experiments of Boehm appear to show that a large proportion of carbonic anhydride is injurious to plants. The author has re-studied the matter, growing plants in glass pots, and passing in, through a tube inserted in the bottom, air enriched to a known extent with carbonic anhydride. In almost all cases the result of supplying the roots and soil with air containing 4, 5, and 12 per cent. of carbonic anhydride was injurious to the plants experimented on, namely, haricots, rye, lupins. Wheat, however, is an exception. It is possible that plants which do not thrive in recently manured soil are particularly susceptible to this action.

J. M. H. M.

The Organic Constituents of Soils. By BERTHELOT and ANDRÉ (*Compt. rend.*, 116, 666—672).—After discussing shortly the origin of humus and the causes of the changes which it undergoes, some analyses of Meudon soils are given. The first series of analyses (1—4) were made with a normal loam, the rest with a sandy soil. The following percentage results refer, in the case of carbon and oxygen, to those portions contained in the organic matter of the soil.

	1.	2.	3.	4.	5.	6.	7.	8.
C	19.1	19.8	22.3	43.5	0.82	1.91	1.78	1.118
H	1.5	—	—	—	—	—	—	—
N	1.7	1.0	1.65	1.7	0.093	0.094	0.14	0.14
O	11.9	—	—	—	—	—	—	—

The results obtained with No. 1 correspond with the formula $C_{13.3}H_{12.7}NO_{6.2}$. The analyses 5—8 were made 10 years ago. By means of vegetation, and owing to the fixation of free nitrogen by soil micro-organisms, the sandy soil has been converted into a true vegetable soil. The weight of nitrogen in the soils and sands amounts to 5 and 6 per cent. (in the richest) and 2 and 3 per cent. (in the poorest) of the total organic matter. Natural kaolins were also found to fix free nitrogen to such an extent that it amounted to as much as 7 per cent. of the total organic matter.

As regards the separation of the various organic constituents of soils, very little is, of course, soluble in water. Distilled water was found to dissolve only 0.1 per cent. of the total nitrogen. Cold dilute acid and alkaline solutions dissolve much more, and at the same time give rise to condensations which have been already discussed.

In the course of experiments on the action of alkalis on soils, it was found that (1) 31.2 per cent. of the total organic carbon was insoluble in alkali, (2) 27.1 per cent. was soluble in alkali and repre-

cipitated by acids, and (3) 40.0 per cent. was dissolved by alkali, but was not precipitated by acids. The percentage of nitrogen in these three portions was 4.0, 5.6, and 9.7 respectively.

Another method employed to isolate the organic matter of soils was to extract with cold hydrofluoric and hydrochloric acids; the residue was well washed and dried in a vacuum. Two soils gave the following results.

	1.	2.
Insoluble matter per cent.	2.56	1.46
Carbon of insoluble matter in 100 parts of total.	61.5	34.3

The percentage composition of the insoluble matter freed from ash and dried at 100° was

	C.	H.	N.	S.	O.
1	55.32	5.29	4.24	0.84	34.31
2	56.58	5.12	3.04	35.26	

The ash (quartz) amounted to (1) 3.52 and 15.58 per cent.

This insoluble substance takes up more or less potash from its solutions, forming two classes of compounds: the one obtained in presence of an excess of potash and rich in alkali, the other by very prolonged washing. Thus 1 gram of the humus, kept for three days with 200 c.c. of 1 per cent. potash, fixed, per cent.,

	1.	2.
K ₂ O	29.4	29.4

Taking into account the amounts of substance dissolved, it was found that 100 parts of insoluble matter rendered insoluble 44 and 42 parts of potash respectively. The insoluble potash salt when washed until free from alkali contained: Carbon, 61.8 and 61.3; hydrogen, 5.7 and 6.1; nitrogen, 4.6; and potash, 6.2 and 3.7 per cent.

The results showing the absorbent property of soils for potash are analogous to those obtained with artificial humic acid (compare Abstr., 1891, 1089).
N. H. M.

Analytical Chemistry.

Origin of Blow-pipe Analysis. By J. LANDAUER (*Ber.*, 26, 898—908).—A purely historical paper.

Estimation of Acids by Calcium Carbonate. By C. FRIEDHEIM and H. LEO (*Pflüger's Archiv*, 51, 615—623).—Polemical. A further reply to Wagner's criticisms (compare Abstr., 1891, 1288).
W. D. H.

Detection of Chlorine, Bromine, and Iodine in Admixture.

By L. F. KEBLER (*J. Anal. Chem.*, **6**, 569—572).—A few drops of nitric acid, sp. gr. 1.42, is added, and the solution warmed gently; it is then cooled, and a few drops of carbon bisulphide added, which will be coloured purple if iodine is present. If the carbon bisulphide only assumes a brownish-yellow tint, bromine is present and iodine absent. If iodine is found, more nitric acid is added, the liquid heated for a few moments and again tested with carbon bisulphide. If the iodine has all been removed, the bromine colour will alone be seen. If bromine is present, more nitric acid is added, and the solution boiled until the bromine is all evolved; the solution is then tested with silver nitrate, when a precipitate soluble in ammonia and insoluble in nitric acid indicates chlorine.

A. J. G.

Estimation of Selenium. By W. MUTHMANN and J. SCHÄFER (*Ber.*, **26**, 1008—1016).—See this vol., ii, 318.

Direct Estimation of Nitrogen in Saltpetre. By A. DEVARDA (*Chem. Zeit.*, **16**, 1952).—The author's process is based on the fact that alkaline solutions of nitrates are reduced by the action of aluminium and zinc powders. Instead, however, of using a mixture of these metals, the author uses an alloy of 45 parts of aluminium, 5 parts of zinc, and 50 parts of copper, which may be readily reduced to powder, and leaves a deposit of metallic copper which will prevent bumping during the subsequent distillation.

The actual process is carried out as follows:—10 grams of the sample is dissolved in a litre of water, and 50 c.c. (= 0.5 gram) is put into a 600 c.c. Erlenmeyer flask and mixed with 60 c.c. of water, 5 c.c. of alcohol, and 40 c.c. of aqueous potash (sp. gr. 1.3). About 2.5 grams of the powdered alloy is added, and the flask is at once connected with a condenser, the end of which dips into the standard acid, at least during the earlier part of the distillation, which may be started after the mixture has been kept at a gentle heat for about half an hour. The process cannot be used in presence of nitrogenous organic matter. If ammonium salts are present, the free ammonia must be first distilled off before adding the reducing alloy. The test analyses prove the great accuracy of the process.

L. DE K.

Estimation of Nitrogen in Urine. By C. ARNOLD and K. WEDEMEYER (*Pflüger's Archiv*, **52**, 590—591).—By using, in Kjeldahl's process, a mixture of 3 parts of sulphuric acid and 1 part of potassium sulphate (Gunning gives 2 : 1, *Zeit. anal. Chem.*, **28**), and adding 1 gram of mercury and copper sulphate during the distillation (Arnold, *Arch. Pharm.*, 1885, 5), 10 c.c. of urine being used, the distillation is complete in 30 to 40 minutes, and the estimation can be completed in an hour. This method is thus considerably quicker than the Schneider-Seegen soda-lime method. It gives rather higher results, but these are considered to be more correct.

W. D. H.

Estimation of Organic Nitrogen. By A. PETIT and L. MONFET (*J. Pharm.* [5], **27**, 297—300).—The nitrogen is converted into

ammonium sulphate by fuming sulphuric acid and mercury, then liberated from this combination by alkaline hypobromite, and measured in the usual way. The process is especially applicable to the determination of the total nitrogen in urine. The acid (5 c.c.) is added drop by drop to the urine (10 c.c.) in a conical flask, the acid liquid brought to the boil, a globule of mercury added, and the boiling continued until the liquid is completely decolorised. This is effected in 15—30 minutes, the longer interval being necessary if albumin is present. After cooling, water (20 c.c.) is gradually added, and then strong aqueous soda, until the acid is nearly neutralised, the temperature not being allowed to rise. The whole is then made up to a definite volume (50 c.c.), and an aliquot portion (10 c.c.) treated with alkaline hypobromite (20 c.c., 35 per cent. of bromine) in a graduated tube in the usual manner, and the volume of nitrogen read off. Trial determinations made with alkaloids, which require, however a much longer time than the less stable compounds, accord very excellently with theory. JN. W.

Gasometric Estimation of Nitrites by means of Schäffer's Reaction. By C. M. VAN DEVENTER (*Ber.*, 26, 958—959).—In a previous paper in connection with this method (this vol., ii, 298), it was stated that about 5 per cent. of the volume of liquid must be added to the volume of nitric oxide. Further experiments indicate, however, that the necessary correction is 3 per cent. The solubility of nitric oxide, which for water is about 5 per cent., is lowered by the presence of salts. The permanganate method gives results about 0.5 per cent. too low on the dissolved nitrite; this the author believes to be due to unavoidable loss of nitrous acid by volatilisation.

A. R. L.

Valuation of Basic Slag. By O. FOERSTER (*Chem. Zeit.*, 16, 1596—1597).—The author states that a really trustworthy process for the estimation of the available amount of phosphoric acid in basic slag is still a desideratum. The best results are obtained when the sample is boiled with dilute sulphuric acid, and the resulting liquid treated according to the molybdate method. L. DE K.

Estimation of Potassium by the Lindo-Gladding Process. By A. F. HOLLEMAN (*Chem. Zeit.*, 16, 1920—1921).—This process consists in evaporating the solution containing the potassium compound with platinic chloride, the excess of which is then removed with alcohol. In order to remove sulphates, the residue is washed with a strong solution of ammonium chloride, which is in turn removed by washing with alcohol (80 per cent. by vol.). The potassium platinocbchloride is then dried and weighed. Breyer and Schweitzer, having tried the process, give it as their opinion that it leads to erroneous results. The author, however, states that, if properly conducted, the process is perfectly trustworthy. L. DE K.

Separation of Calcium and Magnesium from Zinc as Phosphates. By G. C. STONE (*J. Anal. Chem.*, 6, 516—518).—The separation depends on the solubility of zinc phosphate in a mixture of

ammonia and ammonium chloride (strong ammonia, 700 c.c.; ammonium chloride, 100 grams, made up to 1 litre). The cold solution, containing calcium, magnesium, and zinc, is nearly neutralised with ammonia, and 50 c.c. of the ammonia solution and 1 c.c. of a 10 per cent. phosphate solution added for every 0.1 gram of zinc supposed to be present. The precipitate is allowed to settle, filtered, and washed three times with dilute ammonia (1 : 8). The precipitate is dissolved in hydrochloric acid, a little phosphate solution added, and again precipitated with 25 c.c. of the ammonia solution, the precipitate being collected and washed as before. The filtrates and washings are then combined, nearly neutralised with nitric or sulphuric acid, rendered slightly acid with acetic acid, and heated at about 80° until the precipitate crystallises; this is then collected, washed well with hot water, dried, ignited, and weighed as $\text{Zn}_2\text{P}_2\text{O}_7$. If there are but mere traces of calcium and magnesium, one precipitation is sufficient, but two are required if more than 3 or 4 milligrams are present. The amount of ammonia solution used should be proportional to the amounts of these metals; with small amounts, less than the quantities given above will suffice, but with larger amounts it is advisable to use more than 25 c.c. for the second precipitation.

The method is not well adapted for separating very small amounts of zinc from calcium and magnesium, although the results are very satisfactory where the reverse is the case: in the first case, probably the best method would be to precipitate the zinc as sulphide, and then dissolve the precipitate and treat as above. A. J. G.

Estimation of Copper by Volhard's Thiocyanate Method. By R. HENRIQUES (*Chem. Zeit.*, 16, 1597—1598).—This estimation is performed as follows. The copper solution is mixed first with sulphurous acid, and then with a definite quantity of solution of potassium thiocyanate, which should of course be added in excess. After making up to a definite bulk, the liquid is filtered through a dry filter, and an aliquot part of the filtrate is acidified with nitric acid, mixed with ferric sulphate, and the excess of the thiocyanate is titrated back with standard solution of silver nitrate.

The author has, however, not succeeded in getting even approximately correct results, which is not to be wondered at, seeing that a solution of a thiocyanate cannot be acidified with nitric acid without being rapidly decomposed. The process may, however be trusted to give good results if the filtrate is first mixed with excess of silver nitrate, then acidified with nitric acid, and then titrated back with standard solution of thiocyanate with ferric sulphate as indicator.

L. DE K.

Estimation of Mercury in Dilute Solutions of Mercuric Chloride. By L. VIGNON (*Compt. rend.*, 116, 584—586).—Mercury can readily be estimated gravimetrically in the form of sulphide in solutions containing not less than 1 part of mercuric chloride in 1000. 50 c.c. of the solution is mixed with 5 c.c. of pure hydrochloric acid of 22° and 10 c.c. of a clear saturated solution of hydrogen sulphide. Under these conditions, the precipitate forms rapidly, and is easily filtered and washed.

In more dilute solutions, the metal is most readily estimated colorimetrically by adding hydrogen sulphide solution to a known volume of the liquid, and comparing the depth of the brown tint with that produced by mercuric chloride solutions of known strength. Within somewhat wide limits, the intensity of the coloration is simply proportional to the quantity of the mercuric salt present, and a distinct coloration is obtained with 100 c.c. of a solution containing 1 part of mercuric chloride in 240,000 parts of water. C. H. B.

Separation of Iron Oxide from Alumina in Phosphatic Rocks by Fusion with an Alkali Carbonate. By C. GLASER (*J. Anal. Chem.*, 6, 524—526).—The author finds that his process as previously described may give erroneous results when the iron is in excess of the aluminium, but very accurate results are obtained by the following modification.

The hydrochloric acid solution of a phosphorite is nearly neutralised with ammonia, using methyl-orange as indicator, ammonium acetate is added until the colour changes completely from red to pale yellow, and the mixture is then heated on the water bath at a temperature not exceeding 70° until the iron and aluminium phosphates are completely separated. The precipitate is collected, and thoroughly washed with water (not above 70°) by aid of a filter pump. As slight amounts of calcium salts are likely to be retained mechanically, it is advisable to redissolve and precipitate again in the manner described above, first, however, adding a little sodium phosphate to the solution. The mixed phosphates are then heated in a tared platinum crucible, care being taken, however, that the temperature is not high enough to fuse the ferric phosphate. When incineration of the filter is completed, the mass is weighed, then covered with pure sodium carbonate, fused for about 10 minutes over a blast lamp, allowed to cool, and the crucible then placed in a beaker containing a little water. After the melt is moistened, the beaker is heated until the water boils. The cake can now be easily removed from the crucible and transferred to the boiling water without loss. The contents of the beaker are boiled until everything but the ferric oxide is dissolved, then filtered hot, and the residue washed with boiling water. The ferric oxide on the filter, and any that may have adhered to the crucible, is now dissolved in hydrochloric acid, and the iron estimated by precipitation with ammonia in the usual way. To the filtrate from the fusion, which contains everything but the iron, hydrochloric acid is added to expel carbonic anhydride, and the aluminium is then precipitated as phosphate by the addition of ammonium acetate. A. J. G.

Investigation of Potable Water by Schäffer's Nitrite Reaction. By C. M. VAN DEVENTER and B. H. JÜRGENS (*Ber.*, 26, 932—939; compare this vol., ii, 298).—Schäffer has stated that when a few drops of potassium ferrocyanide solution and acetic acid are added to water containing so small a quantity as 1 part in 617,000 of potassium nitrite, a yellow colour is produced, due to the formation of potassium ferricyanide. A solution containing nitrates gives the same

reaction after being heated with lead raspings. The authors confirm these observations.

Making use of the reaction as a test for nitrites in water, it is found that the results are vitiated by the oxygen of air as well as by that dissolved in the water, as the nitric oxide produced in the reaction is thereby oxidised to nitrous anhydride or nitric peroxide, which interact with a further quantity of ferrocyanide. The same objection may be brought against the iodide of starch method; indeed Thresh (*Trans.*, 1890, 185) avails himself of the latter test for the estimation of dissolved oxygen in water. Instead of the apparatus employed by Thresh, the authors keep the water from contact with the air by pouring upon its surface a thin layer of petroleum; this method serves also for Schäffer's test.

To 1 litre of water containing potassium nitrite (0.0006 gram), petroleum was added, and subsequently potassium ferrocyanide (0.1 gram), and about 1 gram of acetic acid; the colourless solution gradually became yellow, the intensity of the coloration being constant at the end of 15 minutes, whilst water containing no nitrite did not exhibit a distinct yellow coloration until the lapse of two hours. Water containing iron, lead, and zinc is boiled with sodium carbonate, and the cooled filtrate tested. Schäffer's test is not less sensitive than the iodide of starch test; it is less influenced than the latter by the presence of hydrogen peroxide. Nitrates have no influence on either process, and the effect of nitric acid is small.

A. R. L.

Estimation of the Hardness of Water by means of Soap. By G. BUCHNER (*Chem. Zeit.*, 16, 1954).—The author calls attention to the fact that, in order to get trustworthy results, the temperature of the water should be exactly 15°. At a higher temperature, a very much larger amount of the soap solution will be required.

L. DE K.

Estimation of Ammonium Thiocyanate in Nitrogenous Manures. By P. L. JUMEAU (*J. Pharm.* [5], 27, 190—193).—A specimen of commercial ammonium sulphate having been found to exercise an injurious influence on vegetation, was examined for thiocyanates, of the ammonium salt of which it proved to contain as much as 9 per cent.

In the presence of chlorides, the sulphates having been removed, the thiocyanates may be estimated by oxidation with potassium permanganate and hydrochloric acid, and precipitation as barium sulphate. In the absence of chlorides, they may be titrated with silver nitrate, using ferric sulphate as an indicator. In the presence of both cyanides and chlorides, they may be titrated with potassium permanganate in the presence of sulphuric acid, the permanganate being standardised against a solution of ammonium thiocyanate of known strength.

JN. W.

Distillation of Mixtures of Water and Alcohol. By E. SOREL (*Compt. rend.*, 116, 693—695).—The tables compiled for the purpose of determining the composition of a mixture of water and alcohol from the composition of the vapours that it evolves differ con-

siderably amongst themselves. Direct experiment shows that the cooling effect of the walls of the retort or still exerts an important disturbing influence, the liquid that trickles down the inner surface of the still containing, as a rule, twice as much alcohol as is present in the boiling liquid.

Experiments made with a retort which was kept at a uniform temperature over the whole of its surface, lead to the construction of the following table, which is intended to replace the older table of Gröning. The strength of the liquid and the distillate are given in Gay-Lussac degrees at 15°.

Boiling liquid.	Vapour.	Boiling liquid.	Vapour.
0°	0°	55°	76·54°
5	35·75°	60	78·17
10	51·00	65	79·92
15	61·50	70	81·85
20	66·20	75	84·10
25	67·95	80	86·49
30	69·26	85	89·05
35	70·60	90	91·80
40	71·95	95	95·05
45	73·45	97·6	97·60
50	74·95		

C. H. B.

Estimation of Sodium Sulphide, Sulphite, and Thiosulphate in Glycerol from Soap Works. By C. FERRIER (*Chem. Zeit.*, 16, 1840).—Glycerol recovered from soap-lyes generally contains from 8 to 10 per cent. of chlorides or sulphates, which seriously affects its commercial value. Should it also contain alkali sulphides, sulphites, or thiosulphates, it becomes an almost useless article. It is, therefore, important for a manufacturer to ascertain their presence and also their quantity. The author now recommends the following process:—

50 grams of the crude sample is diluted with boiled water, neutralised with hydrochloric acid, and made up to 500 c.c. The solution is heated to 60—70° and treated with a few grams of animal charcoal, or better still, with the carbonaceous mass obtained as a bye-product in the manufacture of potassium ferrocyanide, which must, however, be purified by treatment with nitric acid, and by subsequent calcination in a closed crucible. The solution must then be filtered and tested as follows:—

The author uses as test solutions (1) normal iodine solution; (2) a solution of lead nitrate, prepared by dissolving 13·3 grams of normal lead carbonate in a sufficiency of dilute nitric acid, neutralising the excess of acid by means of sodium carbonate, and diluting to 1 litre; (3) an alkaline lead solution prepared by dissolving the same amount of lead carbonate in nitric acid, adding aqueous potash until the precipitated lead hydroxide has dissolved, and making up to 1 litre. 1 c.c. of these lead solutions contains 0·0103 gram of lead, corresponding with 0·0039 gram of sodium sulphide. Before attempting to make a quantitative estimation, it is as well to make

a few qualitative tests. To test for a sulphide, a drop of the solution is put on a paper drenched with lead nitrate. If no coloured spot is formed, the sample contains less than 0.01 per cent. of sulphide. A still more delicate test consists in pouring some of the solution into a flask and mixing it with a few drops of hydrochloric acid and a pinch of sodium hydrogen carbonate. The liquid is then boiled and the vapour allowed to act on a filter-paper moistened with lead nitrate. Even when the sample contains only 0.001 per cent. of sulphide, a yellow stain is formed.

To test for sulphites and thiosulphates, a little of the glycerol solution is mixed with a few drops of solution of barium chloride, which precipitates any carbonate, sulphate, or sulphite. After filtering, the liquid is mixed with a few drops of hydrochloric acid and potassium permanganate. The presence of even 0.01 per cent. of thiosulphate will cause a decided turbidity. To prove the presence of sulphites, the barium precipitate is well washed with boiling water and then suspended in starch solution. A few drops of weak iodine solution are now added, which will cause a very transient blue colour should sulphites be present.

To estimate the sulphides, the lead nitrate solution is added to 25 c.c. of the glycerol solution until precipitation ceases. To see whether enough lead has been added, a drop of the supernatant fluid is put on to lead nitrate paper. The liquid is filtered and mixed with a pinch of sodium hydrogen carbonate and a few drops of starch solution. Iodine solution is now run in until a permanent blue coloration is obtained. This will give the joint amount of sulphites, thiosulphates, and other reducing salts. Another 25 c.c. of the solution is now mixed with the proper amount of lead nitrate, and then with 3 c.c. of a strong solution of strontium chloride. This will cause the precipitation of any carbonates, sulphates, and sulphites, and any thiosulphate will remain in solution, and may be titrated by means of iodine. The difference between the two titrations will give the amount of sulphites. If the sample is free from other reducing agents, such as cyanides, nitrites, or ferrous compounds, the operation would be ended; but as this is never certain, a third titration must be made as follows:—Another 25 c.c. of the sample is mixed with the requisite amount of the alkaline lead solution, filtered, and, after adding 2 c.c. of pure hydrochloric acid, heated to 100°. After cooling, the liquid is neutralised with sodium carbonate, any sulphurous acid is precipitated with strontium chloride, and any iodine now absorbed will represent the other reducing agents, and must be allowed for when calculating the amount of the thiosulphate.

As regards the purification of the glycerol, the author recommends addition of calcium hypochlorite in quantity just sufficient to convert any sulphide, sulphite, or thiosulphate into the more harmless sulphate.

L. DE K.

Detection of Small Quantities of Sugar in Urine. By J. SEEGEN (*Chem. Centr.*, 1893, i, 136—137; from *Pharm. Centrhalte*, 33, 730—731).—The urine is filtered through blood charcoal until completely decolorised. The charcoal is then washed on the filter with distilled water. The charcoal retains colouring matters, uric acid, and

those constituents of the urine which interfere with the separation of the cuprous oxide, so that now the reduction can be observed, not as a yellow coloration, but by the actual separation of the oxide. The washing with water removes some of the sugar retained by the charcoal, so that the second and third wash waters are, practically, aqueous sugar solutions, in which Fehling's solution will detect very minute amounts of sugar. Icteric urine is not decolorised by the use of a layer of blood-charcoal 5—6 cm. high to 20—40 c.c. of urine, but other, even strongly-coloured urines are decolorised by passing twice through the charcoal. Untreated urine containing 0.1—0.5 per cent. of sugar decolorises Fehling's solution without giving any precipitate; after passing through animal charcoal, the liquid gives a yellow turbidity when warmed with Fehling, but the second and third washings of the charcoal give a red precipitate of cuprous oxide. With only 0.05—0.1 per cent. of sugar, a cloudiness is only obtained in the filtrate and the first washings after a little time ($\frac{1}{2}$ —1 minute), whilst the second and third wash-waters do not give any reaction. With still less sugar, it is frequently 10—15 minutes before a reaction occurs, when white flocks of separated phosphates first separate, and on these some yellow points appear; after a time, the whole liquid is coloured yellow.

Urines containing much urates must be strongly acidified with hydrochloric acid, put aside for 24 hours, neutralised, and then treated as above. As normal urine does not give any indication by this test, the occurrence of a reaction must be held to show an amount of sugar above the normal.

A. J. G.

Solubility of Rosin Oil and Mineral Oils, and Mixtures thereof, in Acetone. By E. WIEDERHOLD (*J. pr. Chem.* [2], 47, 394—397; compare Demski and Morawski, *Abstr.*, 1886, 282).—Whilst rosin oil is soluble in acetone in nearly all proportions, mineral oils are either insoluble or only very sparingly soluble. In order that this difference may be available for purposes of evaluation, the acetone must be perfectly dry and free from acid; the presence of aldehyde is not of material importance. All the samples of rosin oil which the author has examined dissolve to a clear solution in half their volume of such acetone at 15°, but only in considerably more if the solvent be not dry. In this connection, the liability of such volatile liquids to condense moisture from the air by the cold of their own evaporation must be remembered, and all vessels containing them must be well stoppered.

The solubility of petroleum in acetone appears to be some sort of function of the specific gravity. Thus for a clear solution at 15°, 1 vol. of burning oil of sp. gr. 0.830 required 4 vols. of acetone; 1 vol. of Russian spindle oil of sp. gr. 0.898 required 40—41 vols.; 1 vol. of "oleonaphtha" of sp. gr. 0.908 required 70—71 vols.

2 c.c. of the sample of oil is shaken with 20 c.c. of acetone at 15° in a cylinder graduated in $\frac{1}{10}$ c.c., and the mixture is allowed to separate for 12—24 hours; under these conditions, a quantity of the oil will be left undissolved, depending on the specific nature of the oil, and varying in the case of Russian lubricating oils from 1.7 c.c. to

0.8 c.c.; the American cylinder oils remain almost entirely insoluble. A table gives the quantities left undissolved in the case of nine Russian oils examined by the author. For thick and unrefined oils, it is necessary to warm the cylinder. The presence of rosin oil in the sample will be detected by the quantity left undissolved being smaller than is normal for an oil of the same designation and gravity. Thus, in the case of an "oleonaphtha" of sp. gr. 0.906, which consisted of Russian spindle oil whose sp. gr. had been raised to that of oleonaphtha by admixture of $\frac{1}{6}$ th of its weight of rosin oil, there was left only 1 c.c. after 2 c.c. had been shaken with 20 c.c. of acetone, whereas genuine oleonaphtha leaves 1.5 c.c.

The test is only trustworthy in the absence of free acids. The author detects free acid in an oil by shaking it with cuprous oxide, and observing if it be coloured green after a lapse of 12 hours.

A. G. B.

Qualitative and Quantitative Wax Analysis. By H. RÖTTGER (*Chem. Zeit.*, 16, 1837—1839).—The author, who has tried every published method for the detection of adulteration of wax, has come to the conclusion that the only trustworthy method is the one recommended by Hübl. This process consists in taking the acidity and the saponification figures, which for pure wax are fairly constant, whilst they differ very much when such substances as tallow, stearic acid, rosin, or paraffins have been added.

The difference between the acidity and saponification figures is called the ether number. The figures for pure wax are: acidity, 20; ether, 75; saponification, 95; and the ratio of the first two is 3.75. For Japan wax, the latter figure is 10; for tallow, 44; for rosin, 0.015; for paraffins, 0, &c., so that a serious adulteration may be detected without the least difficulty.

Benedikt and Mangold take the acidity number of the sample as usual, then saponify another portion with strong aqueous potash, liberate the fatty acids with hydrochloric acid, and, after removing any trace of the latter by repeated boiling with water, they take the acidity number again and call it the saponification figure. The author cannot recommend this modification of the process, as the percentage of wax found in adulterated samples was considerably too high.

L. DE K.

Hübl's Process for testing Wax. By G. BUCHNER (*Chem. Zeit.*, 16, 1922).—This process practically consists of the taking of the acidity and saponification numbers, and is rightly considered to be a safe and elegant method. The author, however, recommends boiling with excess of normal alcoholic potash for at least one hour; otherwise the saponification will not be complete, and the result will be quite untrustworthy.

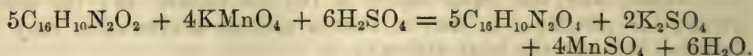
L. DE K.

Detection of Foreign Fats in Wool Fat. By H. HELBING and F. W. PASSMORE (*Chem. Centr.*, 1893, i, 142; from *Pharm. Zeit.*, 37, 704, 712—713).—Wool fat, a cholesterol fat, cannot be saponified by aqueous potash, but is readily saponified by heating at 100° in a

closed vessel with alcoholic potash. The saponification number of lanolin determined in this manner is found to be 83.44. As this is only about one-half of that of ordinary fats, the determination of the saponification number can be applied to the detection of foreign fats in lanolin; paraffins and other hydrocarbons are found in the unsaponified portion, and can be estimated as usual. All the other wool fats, after deduction of the potash value of the free fatty acids contained in them, yield the same saponification number as lanolin. Test analyses are quoted, mixtures of lanolin with oils, fats, and hydrocarbons, and the results appear to be fairly satisfactory.

A. J. G.

Estimation of Indigotin in Commercial Indigo. By O. MILLER (*J. Russ. Chem. Soc.*, **24**, 275—299).—The water in a fair sample of indigo is determined by heating at 100° to constant weight. To estimate the indigotin, a weighed portion (0.5 gram) is thoroughly mixed in a porcelain basin with 10 grams of hydrogen sulphate, H_2SO_4 , not oil of vitriol, and heated on the water-bath for an hour with occasional stirring. In this way all the indigotin is converted into the disulphonic acid, which is then dissolved in water and made up to a litre. 50 c.c. of this solution is diluted with 600 c.c. of water, and titrated with standard potassium permanganate (about 1/280 normal), the colour changing from blue to green, olive, dirty yellow, and finally to a golden-yellow. The disappearance of the olive tint marks the end of the reaction. Pure indigotin gives a pure orange-yellow solution; commercial indigo gives oxidised solutions with either a brownish or reddish tint. The oxidation takes place according to the equation



As indigotin is more readily oxidised, under the conditions of experiment, than indigo-brown, the presence of the latter does not materially interfere with the estimation. Gums, resins, carbohydrates, and albumin, even when added to commercial indigo in quantity, do not appreciably affect the accuracy of the method.

J. W.

Estimation of Theïne in Tea. By N. V. SOKOLOFF (*J. Russ. Chem. Soc.*, **24**, 130).—The method adopted by the author for the estimation of the amount of theïne in tea differs from that ordinarily employed in that, instead of an aqueous extract, a sample of the tea itself is taken, the moisture having been previously ascertained. The tea is moistened with 15—20 drops of alcoholic ammonia, and extracted in a Soxhlet apparatus with chloroform. Subsequently, the chloroform is distilled off, and magnesia added to the residue, which is then extracted three times with boiling water, filtered, and the filtrate evaporated to dryness. The theïne remaining is slightly yellow. To purify it, the aqueous solution is extracted with chloroform, on evaporation of which the theïne is obtained quite colourless.

J. W.

General and Physical Chemistry.

Optical Properties of Liquid Oxygen. By K. OLSZEWSKI and A. WITKOWSKI (*Chem. Centr.*, 1893, i, 595; from *Naturwiss. Rundschau*, 8, 75).—The index of refraction of liquid oxygen is deduced by the authors from the angle of total reflection by means of an apparatus which is described. The relative refractive index of liquid oxygen is thus found to be 1.2232 and the absolute coefficient 1.2235, a value agreeing well with that obtained by Liveing and Dewar, namely, 1.2236. The absorptive power of a column of liquid oxygen of 1 mm. thickness between λ 577 and λ 570, that is, the most intense portion of the yellowish-green absorption band of liquid oxygen, was found to be between 84 and 89 per cent.; whilst for the red absorption band between λ 630 and λ 638, a mean value of 88 per cent. was obtained.

A. R. L.

Refraction Constants of Phosphorus in the Free State, and in its Compounds with Elements or Monovalent Groups. By F. ZECCHINI (*Gazzetta*, 23, i, 97—109).—The author has determined the refraction constants of a number of phosphorus compounds with respect to the line D; the data obtained are summarised in the following table.

Substance.	Temperature.	$P \frac{\mu_D - 1}{d}$.	$P \frac{\mu_D^2 - 1}{d(\mu_D^2 + 2)}$.	Atomic refraction of phosphorus.	
				From n .	From n^2 .
PEt_3	18.6°	67.55	40.24	17.24	9.47
PEt_3, EtI	20.0	110.42	65.44	18.24	10.29
PCl_3 (1) ..	26.1	64.70	37.77	14.45	7.71
PCl_3 (2)	24.4	66.91	38.80	16.65	8.81
POCl_3 (1)	25.1	42.41	25.25	8.92	4.97
POCl_3 (2)	26.6	42.39	25.24	9.60	5.74
PBr_3	26.6	66.03	36.50	20.01	9.72
PI_2 (1)	29.3	74.60	38.13	24.12	9.92
PI_2 (2) ..	24.0	75.03	38.19		

The atomic refractions given under the headings n and n^2 are calculated from the molecular refractions, $P \frac{\mu - 1}{d}$ and $P \frac{\mu^2 - 1}{(\mu^2 + 2)d}$ respectively; the values employed in calculating from the simpler formula are those previously given by the author (this vol., ii, 253), whilst Conrady's values are used in working from the theoretical formula. Triethylphosphine, phosphorus tribromide, and phosphorus oxychloride were examined in the pure state; triethylphosphonium iodide was employed in a 14.6034 per cent. aqueous solution, whilst,

with phosphorus pentachloride, determinations (1) and (2) were made with 6.5171 and 6.0775 per cent. carbon bisulphide solutions respectively. In boiling carbon bisulphide, phosphorus diiodide has a molecular weight corresponding with the formula P_2I_4 ; carbon bisulphide solutions containing (1) 7.1896 and (2) 6.3215 per cent. of the iodide were used in the determinations.

The author concludes that the atomic refraction of phosphorus varies very considerably with the nature and number of the other elements with which it is combined; the value is least in the chlorides of phosphorus and greatest in the iodide, the value deduced from the bromide being intermediate. Hydrogen phosphide gives a much lower value for the atomic refraction of phosphorus than do the halogen compounds of the same type. Compounds of phosphorus with the same elements give practically the same values for the atomic refraction; this is especially well shown with the tri- and pentachlorides. The very low refraction equivalent of phosphorus oxychloride is remarkable; it gives the atomic refraction of phosphorus as less than half that which the element has in the free state or when combined with chlorine alone. It is noteworthy that with these com-

pounds the formula $\frac{P\mu-1}{d}$ gives as a rule more consistent results than the theoretical formula.

W. J. P.

Refraction Constants of the Acids of Phosphorus and their Sodium Salts. By F. ZECCHINI (*Gazzetta*, 23, i, 109—120; compare preceding abstract).—The author has measured the refraction constants, with reference to the D-line, of phosphoric, metaphosphoric, pyrophosphoric, phosphorous, and hypophosphorus acids, and their sodium salts in aqueous solution. The atomic refraction of phosphorus deduced from the molecular refraction of the sodium salts cannot be entirely depended on, owing to the arbitrary values which must be assigned to the metal; the numbers obtained from the refractive indices of the acids are given in the following table, together with Thorpe and Tutton's value for phosphorus oxide (*Trans.*, 1890, 545).

	Atomic refraction of phosphorus obtained from formula.	
	n .	n^2 .
P_4O_6	9.71	5.33
HPO_3	5.94	2.77
H_3PO_4	4.08	1.46
H_3PO_3	5.18	2.46

It is noteworthy that a much higher value for the atomic refraction is obtained from the oxide than from the acids or salts.

W. J. P.

Influence of Temperature on the Rotatory Power of Liquids. By A. AIGNAN (*Compt. rend.*, 116, 725—727).—The author points out that where a liquid is optically inactive because it is a mixture of

two active substances of opposite rotatory powers, the inactivity will, as a rule, hold only for rays of a certain wave-length, and the mixture will be active in one direction for rays of shorter wave-length and active in the opposite direction for rays of greater wave-length. This phenomenon is well shown by mixtures of lævogryate terebenthene and dextrogyrate camphene.

Similarly a change in the temperature of such liquids will disturb the optical equilibrium, and the liquid will become active in one direction when the temperature rises and in the other when the temperature falls. This phenomenon also is observed with the mixture of terebenthene and camphene, and with red rays the rotatory power changes in sign between 61° and 73° , and with yellow rays between 13° and 33° , whilst with green rays the liquid is always dextrogyrate between 13° and 90° , but the rotatory power increases with the temperature.

Phenomena of this kind were observed by Biot in the case of solutions of tartaric acid. The author suggests that the liquids examined by Colson (this vol., ii, 255) are mixtures of two substances of opposite optical activities, and that the variations observed in the rotatory power are due to the causes specified above.

C. H. B.

Meidinger's Cells. By A. A. KRAKAU (*J. Russ. Chem. Soc.*, 24, 325—330).—The author undertook an investigation of cells of the Meidinger type used in telegraphic practice with a view to ascertain which form was most suitable, and to study the E.M.F., efficiency, &c., of each. He found, however, great variations in the results obtained with precisely similar elements, so that he was unable to arrive at any definite conclusions, except that unknown secondary reactions play a very important part in the working of the elements.

J. W.

Leclanché Battery. By A. DITTE (*Compt. rend.*, 116, 812—815).—When a couple formed of a rod of zinc and a plate of platinum is immersed in a 10 per cent. solution of sodium chloride, the zinc becomes covered with a layer of zinc hydroxide, which, at some distance down the rod, spreads out and forms a kind of diaphragm, which separates the liquid into two parts of different composition, the upper section being strongly alkaline and containing no zinc, whilst the lower is neutral and contains zinc chloride.

Since the heat of formation of zinc oxide is greater than that of water, the zinc decomposes the water, but the action is at once arrested by the formation of a superficial film of zinc oxide, insoluble in water or a solution of sodium chloride. The decomposition of sodium chloride solution by the zinc platinum couple is also exothermic, and zinc chloride and sodium hydroxide are formed. The dilute solutions of the latter being lighter than the salt solution, there is an upward current of sodium hydroxide solution along the surface of the platinum plate, and a downward current of zinc chloride solution from the zinc rod. The zinc hydroxide is formed by the interdiffusion of these two currents.

If the platinum plate is replaced by a mass of manganese peroxide,

polarisation is greatly reduced, and the layer of liquid which the current has to traverse is also much thinner; consequently, the action is more rapid and the phenomena are more marked. In the ordinary battery, the sodium hydroxide solution is retained in the porous cell, and no zinc hydroxide is formed in the outer liquid until the alkaline solution escapes.

C. H. B.

Abnormal Electromotive Forces of Mercury. By H. BRANDENBURG (*Zeit. physikal. Chem.*, **11**, 552—576).—The electromotive force of an element of the type $\text{Zn} \mid \text{H}_2\text{SO}_4 \mid \text{Hg}$ is greatly diminished by the addition of a few drops of potassium iodide solution to the liquid. Potassium bromide and chloride exercise the same influence in a less degree, whilst potassium sulphide reduces the difference of potential from 1.4 to about 0.2 volt. The author has investigated a large number of substances with regard to this property, and finds the following salts show it to a greater or less extent: potassium sulphide, cyanide, thioacetate, selenocyanate, thiocyanate, chloride, bromide, iodide, nitrite, ferrocyanide, and sodium selenothiosulphate, thioglycollate, thiosulphate, thiophenolate, and sodium succinimide. The action of these substances is due to their removing mercury ions, which are present in the sulphuric acid in small quantity, either by forming insoluble compounds with them, or by producing double salts, from which mercury is not dissociated as an ion.

J. W.

Electrical Conductivity of Mixtures. By D. KONOVALOFF (*J. Russ. Chem. Soc.*, **24**, 440—450).—The author has determined the electrical conductivity of mixtures of weak bases, such as aniline, with weak acids, such as acetic acid. The bases investigated were aniline, methylaniline, dimethylaniline, and toluidine; the acids were acetic, propionic, and butyric. Measurements were made at 21°, and, in the case of mixtures of aniline with acetic acid, also at 16°. The results are given in tables and in a series of curves made by tabulating the percentage composition of the mixture as abscissa against the electrical conductivity as ordinate. For each pair of substances, the conductivity starts from the neighbourhood of zero for the pure amine, rises to a maximum as acid is added, and then diminishes to zero again for the pure acid. The composition of the mixture, expressed as molecules of amine in 100 mols. of mixture, which gives the maximum conductivity at 21°, is exhibited in the following table, as well as the maximum value in mercury units multiplied by 10⁶.

Base.	Acid.	Composition.	Maximum value.
Aniline	Acetic.....	14.0	27.0
Methylaniline...	„	14.3	28.7
Toluidine.....	„	14.0	18.4
Dimethylaniline.	„	12.0	22.1
Aniline.....	Propionic...	31.0	6.7
„	Butyric.....	35.0	1.0

J. W.

Electrical Conductivities of Phosphoric acid and of Alkali Phosphates. By D. BERTHELOT (*Ann. Chim. Phys.* [6], 28, 5—28).

—This paper contains the author's measurements of the electrical conductivities of phosphoric acid and of sodium, potassium, and ammonium mono-, di-, and tri-phosphates. The conclusions deduced from the results as to the basicity of phosphoric acid have been already given (Abstr., 1892, 395). A. R. L.

A small Air Thermometer for Laboratory Use. By L. MEYER (*Ber.* 26, 1047—1051).—A modification of the apparatus devised by Bottomley (*Phil. Mag.* [5], 26, 149). J. B. T.

Melting Point Determinations. By E. HAASE (*Ber.*, 26, 1052—1054).—The melting points of the following substances were determined by the air thermometer described by L. Meyer (preceding abstract). The freezing mixture employed consisted of solid carbonic anhydride and anhydrous ether; the lowest temperature observed was -75° — -78° . Chlorobenzene, -44.9° ; bromobenzene, -31.1° ; iodobenzene, -29.8° ; orthochlorotoluene, -34° ; metachlorotoluene, -47.8° ; parachlorotoluene, $+7.4^{\circ}$; orthobromotoluene, -25.9° ; metabromotoluene, -39.8° ; parabromotoluene, $+28.2^{\circ}$; chloroform, -62° ; trichloronitromethane, -64° ; ethylenic chloride, -42° ; benzylic chloride, -48° ; trichlorotoluene, -22.5° ; benzaldehyde, -26° ; zinc methide, -40° ; zinc ethide, -28° ; titanium chloride, -25° ; arsenic chloride, -16° .

The following substances become viscid and turbid at -75° :—methylic valerate, ethylic valerate, propylic valerate, amylic normal butyrate. The following substances are clear, but more or less viscid, at the same temperature: amylic formate, amylic acetate, amylic valerate, isobutylic formate, isobutylic acetate, ethylic normal butyrate, methylic propionate, and ethylic propionate; methoxybenzene and ethoxybenzene are gelatinous. Methylic formate, propylic formate, methylic acetate, ethylic acetate, propylic acetate, ethylic chloride, ethylenic chloride, ethylenic chlorobromide, methylic bromide, trimethylenic bromide, carbon oxychloride, silicon tetrachloride, and sulphur monochloride are unaltered at -75° .

J. B. T.

Thermochemistry of the Ions. By W. OSTWALD (*Zeit. physikal. Chem.*, 11, 501—514).—From the electromotive force of cells into which various metals enter, and from Thomsen's thermochemical data, the author calculates the following "heats of ionisation," that is, the heat change on the conversion of free metal into metallic ions.

	Atom.	Equivalent.
Potassium	+ 61.0 Cal.	+ 61.0 Cal.
Sodium	+ 56.3 "	+ 56.3 "
Lithium	+ 62.0 "	+ 62.0 "
Strontium	+ 115.5 "	+ 57.8 "
Calcium	+ 107.0 "	+ 53.5 "
Magnesium	+ 106.7 "	+ 53.4 "
Aluminium	+ 117.5 "	+ 39.2 "

	Atom.	Equivalent.
Manganese	+ 48.1 Cal.	+ 24.0 Cal.
Iron (ferrous ions)	+ 20.0 "	+ 10.0 "
„ (ferrous into ferric) ..	- 12.1 "	- 12.1 "
Cobalt	+ 14.6 "	+ 7.3 "
Nickel	+ 13.5 "	+ 6.8 "
Zinc	+ 32.6 "	+ 16.3 "
Cadmium	+ 16.2 "	+ 8.1 "
Copper (cupric ions)	- 17.5 "	- 8.8 "
„ (cuprous ions)	- 17.0 " (?)	- 17.0 "
Mercury	- 20.5 "	- 20.5 "
Silver	- 26.2 "	- 26.2 "
Thallium	+ 1.0 "	+ 1.0 "
Lead	- 1.0 "	- 0.5 "
Tin	+ 2.0 "	+ 1.0 "

All the metals that easily form ions have positive heats of ionisation; the others have negative heats of ionisation. J. W.

Thermochemistry of α -Dibromopropionic acid. By S. TANATAR (*J. Russ. Chem. Soc.*, **24**, 365—371).—Heat of solution of α -dibromopropionic acid at $13^\circ = 1.64$ Cal.

Heat of neutralisation with potash at 14 — $16^\circ = 14.85$ Cal. There is no thermal effect when the normal potassium salt of α -dibromopropionic acid is mixed with excess of dilute alkali or excess of the dilute acid.

There is an evolution of 0.464 Cal. when equivalent quantities of decinormal solutions of potassium chloride and α -dibromopropionic acid are mixed, and an absorption of 0.544 Cal. when equivalents of hydrogen chloride and potassium α -dibromopropionate are taken. The heat effect if either acid completely displaced the other from its salts would be 1.106 Cal., evolution in the one case and absorption in the other.

The heat of dissolution of the salt $KC_3H_3Br_2O_2 + H_2O$ at 14° is -2.878 Cal., and of the anhydrous salt $+0.518$ Cal., so that the heat of hydration is $+3.396$. The heat of dissolution of the acid salt $KC_3H_4Br_4O_4$ is -7.91 Cal.

The heat of neutralisation of propionic acid with potash is $+13.46$ Cal.; its heat of dissolution, $+0.604$ Cal.; and that of its potassium salt, $+2.74$ Cal. J. W.

Thermochemical Investigation of Ureides derived from Acids containing 1 and 2 Carbon Atoms. By C. MATIGNON (*Ann. Chim. Phys.* [6], **28**, 70—125).—The general mode of procedure adopted in this and subsequently published memoirs (following abstracts) is to determine the heats of combustion of the compounds by means of the calorimetric bomb and deduce from these data their heats of formation.

The heat of neutralisation of carbamide by nitric acid is very small and indicates that the nitrate is almost completely dissociated; in a concentration corresponding to $\frac{1}{24}$ mol. per litre, the value is *nil*,

whilst in a concentration of $\frac{1}{8}$ mol. per litre it is +0.13 Cal. When carbamide nitrate ($\frac{1}{8}$ mol.) is dissolved in water (1 litre), an absorption of 10.7 Cal. is observed. The heats of dissolution of solid carbamide (-3.6 Cal.) and of solid nitric acid (+6.6 Cal.), lead to the relation:— HNO_3 sol. + CON_2H_4 sol. = $\text{CON}_2\text{H}_4, \text{HNO}_3$ sol. +13.8 Cal. This value is much smaller than those corresponding with the most feeble inorganic bases. Aniline is a much stronger base; its solution, saturated with nitric acid, should give +7.4 Cal., whilst carbamide only furnishes +0.2 Cal.

Ethylcarbamide. Heat of combustion at constant volume, +471.9 Cal., and at constant pressure, +472.2 Cal. Heat of formation:— C_2 diamond + O + N_2 gas + H_2 gas = $\text{CON}_2\text{H}_3\text{Et}$ sol. +86.7 Cal. The heat of dissolution of ethylcarbamide at 14° in a concentration of $\frac{1}{24}$ per litre is -2.3 Cal. The difference in the heats of combustion of carbamide and of ethylcarbamide is +320.7 Cal., a value abnormally large. The formation of ethylcarbamide from liquid alcohol and solid carbamide develops +3.8 Cal.

Thiocarbamide. Heat of combustion at constant volume, +341.9 Cal., and at constant pressure, +342.8 Cal. Heat of formation, +30.5 Cal. Heat of dissolution at 10° in a concentration of $\frac{1}{2}$ equivalent per litre, -5.33 Cal. The displacement of sulphur by oxygen in thiocarbamide develops +50.3 Cal. The heat of neutralisation of thiocarbamide by nitric acid at 11° in a concentration of $\frac{1}{4}$ mol. per litre of water is +0.02 Cal. (carbamide gives +0.24 Cal.). Heat of dissolution of thiocarbamide nitrate is -8.5 Cal. HNO_3 sol. + CSN_2H_4 sol. = $\text{CSN}_2\text{H}_4, \text{HNO}_3$ sol. +9.8 Cal. The displacement of oxygen by sulphur in carbamide diminishes the basic function, and it would appear from this that sulphur is more negative than oxygen; thiocarbamide has, however, no acidic function, its heat of dissolution in water and potash being identical.

Ammonium thiocyanate. Heat of combustion at constant volume, +344 Cal., and at constant pressure, +345 Cal. Heat of formation, +28.4 Cal. The transformation of this compound into thiocarbamide develops +2.1 Cal.

Guanidine and its Salts (Abstr., 1892, 1142).

Ureides of Normal Acids (Abstr., 1891, 1448).

Ureides of Mono- and Poly-basic Acids containing 2 Carbon Atoms.—

Hydantoin:—Heat of combustion at constant volume, +312.4 Cal., and at constant pressure, +311.9 Cal. Heat of formation, +109 Cal. The formation of hydantoin from glycollic acid and carbamide develops +5.6 Cal. Heat of dissolution in water at 11° in a concentration of $\frac{1}{25}$ mol. per litre is -6.1 Cal., or in potash, +0.5 Cal. Carbamide glycollate is obtained in the form of white crystals, insoluble in ether, by evaporating mixed solutions of carbamide and glycollic acid. Its heat of dissolution in water at 17° in a concentration of $\frac{1}{10}$ mol. per litre is -8.2 Cal. De Forcrand gives -2.8 Cal. as the heat of dissolution of glycollic acid; consequently $\text{C}_2\text{H}_4\text{O}_3$ sol. + CON_2H_4 sol. = $\text{CON}_2\text{H}_4, \text{C}_2\text{H}_4\text{O}_3$ sol. +2 Cal. Heat of formation of carbamide glycollate, -243.4 Cal. The formation of hydantoin from carbamide glycollate:— $\text{CON}_2\text{H}_4, \text{C}_2\text{H}_4\text{O}_3$ sol. = $\text{C}_3\text{H}_4\text{N}_2\text{O}_2$ sol. + $2\text{H}_2\text{O}$ + 36 Cal.

Carbamide combines with glycocine with scarcely any appreciable development of heat, and the product, *carbamide amidoacetate*, forms large, lustrous crystals, and completely dissociates in water. Its heat of dissolution at 12° in a concentration of $\frac{1}{32}$ mol. per litre is -6.4 Cal.; consequently:— CON_2H_4 sol. + $\text{C}_2\text{H}_5\text{NO}_2$ sol. $\text{CON}_2\text{H}_4, \text{C}_2\text{H}_5\text{NO}_2$ sol. $+0.8$ Cal. The direct formation of hydantoin from carbamide amidoacetate would involve the absorption of -14.6 Cal.

Hydantoic acid.—Heat of combustion at constant volume, $+308.9$ Cal., and at constant pressure, $+308.4$ Cal. Heat of formation, $+181.6$ Cal. It is a monobasic acid. Heat of dissolution in potash, $+6.8$ Cal.; excess of potash does not alter this value. The heat of dissolution in water is about -6.5 Cal., so that the heat of neutralisation of the dissolved acid must be about $+13$ Cal., the ordinary value observed with monobasic acids. The conversion of hydantoin into hydantoic acid:— $\text{C}_3\text{H}_4\text{N}_2\text{O}_2$ sol. + H_2O sol. = $\text{C}_3\text{H}_6\text{N}_2\text{O}_3$ sol. develops $+2.2$ Cal. In the presence of potash:— $\text{C}_3\text{H}_4\text{N}_2\text{O}_2$ diss. + KOH diss. = $\text{C}_3\text{H}_5\text{KN}_2\text{O}_3$, develops 8.8 Cal.

Allantoin (Abstr., 1891, 1448). Methylallantoin. Heat of combustion at constant volume, $+567.7$ Cal., and at constant pressure, $+566.9$ Cal. Heat of formation, $+180.6$ Cal. The difference between the heats of combustion of allantoin and methylallantoin ($+153.1$ Cal.) is normal.

Ureides of Oxalic acid.—Parabanic and Oxaluric acids (Abstr., 1891, 1449). Oxamic acid. Heat of combustion at constant volume, $+129.5$ Cal., and at constant pressure, $+128.8$ Cal. Heat of formation, $+163.3$ Cal.

Dimethylparabanic acid. Heat of combustion at constant volume, $+539.1$ Cal., and at constant pressure, $+538.6$ Cal. Heat of formation, $+139.9$ Cal. The difference between the heats of combustion of dimethylparabanic and of parabanic acids, $+326$ Cal., gives $+163$ Cal. as the difference for each methyl group, a value abnormally large.

A. R. L.

Thermochemical Investigation of Polybasic Ureides and of Uric acid. By C. MATIGNON (*Ann. Chim. Phys.* [6], 289—394).—When alloxantin is heated on the water-bath with sulphuric acid, and an equal volume of water added, a yellowish compound separates which, on boiling with water, is converted into a mixture of parabanic and barbituric acids (Finck, *Annalen*, 132, 304). This compound is *oxalylmalonic diureide*, $\text{C}_7\text{H}_4\text{N}_4\text{O}_6$. Barbituric acid (malonic ureide). Heat of combustion at constant volume, $+354.2$ Cal., and at constant pressure, $+353.4$ Cal. Heat of formation, $+161.8$ Cal. Grimaux has synthesised the acid by heating together malonic acid and carbamide:— $\text{C}_3\text{H}_4\text{O}_4$ sol. + CON_2H_4 sol. = $\text{C}_4\text{H}_4\text{N}_2\text{O}_3$ sol. + $2\text{H}_2\text{O}$ $+8.2$ Cal. The formation of barbituric acid is considerably more exothermic than that of the oxalic ureides, the syntheses of which have not been effected. Acid malonic ureide, $\text{C}_3\text{H}_4\text{O}_4, \text{CON}_2\text{H}_4$, is obtained in colourless, anhydrous crystals when a solution of malonic acid and carbamide is allowed to evaporate over sulphuric acid. The heat of combustion at constant volume is $+357.2$ Cal., and at constant pressure, $+356.3$ Cal. Heat of formation, $+296.9$ Cal. Its forma-

tion from solid malonic acid and solid carbamide develops +2.5 Cal. It decomposes into barbituric acid and water:— $\text{C}_3\text{H}_4\text{O}_4, \text{CON}_2\text{H}_4$ sol. = $\text{C}_4\text{H}_4\text{N}_2\text{O}_3$ sol. + $2\text{H}_2\text{O}$ sol. +5.7 Cal. A neutral malonic ureide could not be prepared. Barbituric acid has two acidic functions, of which the first is stronger than that of the normal carboxylic acids and of the same order as that of picric acid; whilst the second acidic function is very feeble, more so than the third function of phosphoric acid; the corresponding salts are decomposed by water.

Alloxan (Abstr., 1891, 1448). The heat of combustion of mesoxalic acid at constant volume is +129.4 Cal., and at constant pressure, +128.3 Cal.; the heat of formation is +292.7 Cal. The formation of alloxan from the acid and carbamide (solid) develops

+1.2 Cal. Dialuric acid (tartronic ureide), $\text{CO} < \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix} > \text{CH}\cdot\text{OH}$, oxidises so rapidly in the air that no constant values could be obtained with it. The heat of combustion of tartronic acid at constant volume is +166.6 Cal., and at constant pressure, +165.8 Cal. The heat of formation is +165.8 Cal. The formation of dialuric acid from carbamide and tartronic acid (solid) would develop +4.2 Cal.; its heat of formation is +201.1 Cal. (approx.).

Uramile (amidomalonic ureide), $\text{CO} < \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix} > \text{CH}\cdot\text{NH}_2$. Heat of combustion at constant volume, +380 Cal., and at constant pressure, +379 Cal. Heat of formation, +170.7 Cal. Thionuric acid, $\text{CO} < \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix} > \text{CH}\cdot\text{NH}\cdot\text{SO}_3\text{H}$, was discovered by Liebig and Wöhler.

It is partially hydrolysed in aqueous solution into uramile, but may be obtained in acicular crystals by evaporating its aqueous solution over concentrated sulphuric acid. Its aqueous solution causes a brisk evolution of hydrogen on the addition of zinc or cadmium, and decomposes carbonates in the cold. The author describes at length its mon- and di-acid salts; they are crystalline compounds which rapidly become red in the air.

Alloxantin (Abstr., 1891, 1448). Amalic acid (tetramethylalloxantin). Heat of combustion at constant volume, +1241.9 Cal., and at constant pressure, +1240.6 Cal. Heat of formation, +374 Cal. Hydurilic acid, $\text{C}_8\text{H}_6\text{N}_4\text{O}_6$ (Ber., 9, 1102). Heat of combustion at constant volume, +660.5 Cal., and at constant pressure, +658.5 Cal. Heat of formation, 302.9 Cal. Baeyer regards this compound as a diureide resulting from the combination of barbituric and dialuric acids. The interaction of the solid acids would develop +10.3 Cal., and the author has effected the synthesis of hydurilic acid by heating together barbituric and dialuric acids.

Deoxyamalic acid is best prepared by heating amalic acid in a sealed tube at 180—185° for three hours. Its heat of combustion at constant volume is +1322.6 Cal., and at constant pressure, +1321.8 Cal. Heat of formation, +292.8 Cal. The difference between the heats of combustion of deoxyamalic acid and amalic acid indicates that the latter is the dihydroxy-derivative of the former. Murexide. Heat of combustion at constant volume, +738.8 Cal., and at constant pressure, +736.7 Cal.

Uric acid. Heat of combustion at constant volume, +462.7 Cal., and at constant pressure, 461.4 Cal. (see also Stohmann, Abstr., 1892, 6). Heat of formation, +148.1 Cal. The oxidation of uric acid in the animal organism has been shown by numerous observers to be incomplete. The various hypotheses claiming to explain the formation of uric acid in the animal organism are then discussed at length; thermic measurements of the salts of uric acid are also given. Pseudouric acid. Heat of combustion at constant volume, +455.2 Cal., and at constant pressure, +454 Cal. Heat of formation, +224.5 Cal. The transformation of pseudouric acid into uric acid (solid compounds) is endothermic (−6 Cal.). Isouric acid. Heat of combustion at constant volume, +460.6 Cal., and at constant pressure, +459.4 Cal. Heat of formation, +150.1 Cal. The transformation of uric acid into isouric acid (solid compounds) would give rise to the development of +2 Cal., a value too small to enable the change to be actually effected.

Theobromine. Heat of combustion at constant volume, +846.45 Cal., and at constant pressure, +846 Cal. Heat of formation, +90.1 Cal. Caffeine. Heat of combustion at constant volume, +1016.5 Cal., and at constant pressure, +1016 Cal. Heat of formation, +83.4 Cal. Since the introduction of a methyl group, combined with nitrogen, raises the heat of combustion of a compound about +165 Cal. (see next abstract), this value has been calculated for xanthine from those given above for caffeine and theobromine. The heat of combustion of xanthine is thus found to be +518.5 Cal., and its heat of formation +91 Cal.

Thiohydantoïn. Heat of combustion at constant volume, +502.4 Cal., and at constant pressure, +503 Cal. Heat of formation, +58.9 Cal. Thiohydantoïc acid. Heat of combustion at constant volume, +497.9 Cal., and at constant pressure, +498.5 Cal. Heat of formation, +132.4 Cal.

A. R. L.

General Results of the Thermochemical Study of the Ureïdes. By C. MATIGNON (*Ann. Chim. Phys.* [6], 28, 498—528).—The fact that the heat of combustion of orthotoluidine is approximately the same as that of metatoluidine, whilst that of methylaniline is greater, led Petit (*Ann. Chim. Phys.* [6], 18, 145) to conclude that the introduction of a methyl group into the side chain is a less exothermic phenomenon than the introduction of such a group into the benzene nucleus. The author's results confirm this. He compares the heats of combustion (given in the preceding abstracts) of certain ureïdes, and finds that the displacement by methyl of an atom of hydrogen combined with nitrogen raises the heat of combustion of the compound by 164—165 Cal., whilst the displacement by methyl of an atom of hydrogen combined with carbon raises the heat of combustion at most 157 Cal. The primary amines have a lower heat of combustion than the secondary or tertiary amines isomeric with them. The heat of combustion of the residue = $\text{CH}_2\text{:—C (diamond)} + \text{H}_2\text{ gas} + \text{O}_3 = \text{CO}_2 + \text{H}_2\text{O} \dots + 163.3 \text{ Cal.}$, leads to the conclusion that the heat of formation of a compound is increased by 6—7 Cal. when methyl is substituted for one of the hydrogen atoms combined

with carbon, and is diminished by 1—2 Cal. when one of its hydrogen atoms in combination with nitrogen is displaced by methyl.

The above law indicates that metameric compounds exist which present notable differences in their heats of formation, and it renders possible, in many cases, the molecular migration of alkyl groups in combination with nitrogen to a carbon atom. It can, therefore, be used to establish the constitution of a compound.

Nitroguanidine has a heat of combustion at constant volume +211.4 Cal.; and at constant pressure +210.3 Cal. The heat of formation is +22 Cal. A study of this compound indicates that the formation of nitro-derivatives is less exothermic when the nitro-group enters into combination with a nitrogen atom; it is, therefore, to be expected that such nitro-derivatives will be the more powerful explosives.

The introduction of an alkyl group into a compound seems to diminish the positive work necessary to effect its dissolution.

The research has led to the deduction of certain rules, which will serve for the synthesis of new ureides.

A. R. L.

Graphical Treatment of some Thermodynamical Problems on Conditions of Equilibrium in Salt Solutions with Solid Phases. By A. C. VAN RIJN VAN ALKEMADE (*Zeit. physikal. Chem.*, **11**, 289—327).—An application of the thermodynamical principles of Gibbs to the consideration of some special cases of conditions of equilibrium in salt solutions.

H. C.

Determination of the Specific Gravity of Salts Soluble in Water. By J. W. RETGERS (*Zeit. physikal. Chem.*, **11**, 328—344).—In determining the specific gravity of salts soluble in water, the author has formerly employed, with advantage, the method of suspension in liquids so adjusted, that their specific gravities equal those of the salts taken. As only few liquids have hitherto been found available for the above purpose, attention has now been devoted to obtaining new liquids of high specific gravity for use in the determinations. In the first place, attempts were made by dissolving various metallic iodides in methylenic iodide to effect an increase in the specific gravity, 3.324 at 16°, of this liquid. Only in three cases was an appreciable increase noticed, these being with stannic iodide, 3.481 at 10°, with arsenious iodide, 3.449 at 12°, and with antimonious iodide, 3.453 at 12°. A mixture of stannic and arsenious iodides, dissolved in methylenic iodide, gave a liquid of specific gravity 3.610 at 12°, and by using a mixture of stannic and antimonious iodides a specific gravity of 3.63 was obtained. Experiments were then made with arsenic tribromide, a compound melting at 20° to a nearly colourless liquid of specific gravity 3.540 at 25°. By dissolving trihaloids of antimony and bismuth in this, heavier liquids were obtained, the highest observed specific gravity being 3.80 in the case of a mixture of arsenious and antimonious iodides in arsenious bromide; this liquid solidifies, however, at 31°. By mixing solutions of arsenious and antimonious iodides in arsenious bromide with those in methylenic iodide, a liquid was obtained of specific gravity 3.702,

which only solidifies at 20° ; it has, however, the disadvantage of being opaque. A liquid which does not solidify at the ordinary temperature, and was the heaviest observed fulfilling this condition, was obtained by mixing stannic iodide and arsenious bromide. The specific gravity is 3.731 at 15° , but the solution is opaque. H. C.

Dissociation of Saline Hydrates and Analogous Compounds.

By H. LESCŒUR (*Ann. Chim. Phys.* [6], 28, 237—256).—A continuation of the author's researches on this subject (Abstr., 1889, 815; *Ann. Chim. Phys.* [6], 19, 35, 533; 21, 511; 25, 423). The compounds examined in this memoir are the so-called acid acetates; they include additive compounds of sodium, potassium, lithium, and thallium acetate with acetic acid, and of sodium and potassium trichloroacetate with acetic acid. They are analogous to saline hydrates, being formed by direct addition of acetic acid. They lose acetic acid at the ordinary temperature by a phenomenon analogous to efflorescence, but unlike the saline hydrates, which do not effloresce when their tension of dissociation is lower than that of the atmospheric aqueous vapour, the acid acetates lose acetic acid in the atmosphere, whatever be their tension of dissociation. This is because the atmosphere does not contain acetic acid vapour, as it does aqueous vapour, which limits the dissociation of the hydrates. A. R. L.

Determination of the Electrolytic Dissociation of Salts by means of Solubility Experiments. By S. ARRHENIUS (*Zeit. physikal. Chem.*, 11, 391—402).—The discrepancy observed by Noyes between the numbers obtained for the degree of dissociation of dissolved salts from his solubility experiments (Abstr., 1892, 1143), and those derived from the electrical conductivities, and more especially the opinion which this investigator has expressed, that the former series of numbers is more trustworthy than the latter, and that water takes a part in the electrolysis of a salt solution, has induced the author to submit this question to an experimental examination. He finds that the electrolytic dissociation, calculated from the solubility, differs enormously in the case of the same salt, for example, silver nitrate, according to whether the sparingly soluble salt with which this is combined is more or less soluble. No agreement, therefore, can be obtained between numbers which apply to one and the same salt, so that solubility experiments do not give trustworthy results for the determination of the electrolytic dissociation. The cause of this is, seemingly, that the law of mass action, upon which the calculation of the experimental results is based, is not applicable to strongly dissociated electrolytes. H. C.

Electrolytic Dissociation of Water. By J. J. A. WIJS (*Zeit. physikal. Chem.*, 11, 492—494).—Methylic acetate and water react to form methyl alcohol and acetic acid (or an acetate) at a rate proportional to the number of hydrogen ions or hydroxyl ions present in the solution. The reaction conditioned by the hydroxyl ions (saponification by a base) proceeds much more rapidly than that conditioned by the hydrogen ions (catalysis by an acid). Water behaves both as a weak base and also as a weak acid, so that it is assumed to be slightly

dissociated into hydrogen ions and hydroxyl ions $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$. To measure the extent of this dissociation, the author prepared an aqueous solution of methylic acetate, carefully sterilised and freed from acid impurity, and from time to time titrated it with standard alkali in order to ascertain the amount of acetic acid liberated. The action was supposed to be caused entirely by the hydroxyl ions, and only the first few titrations were considered, as the free acetic acid contributes a considerable number of hydrogen ions as the decomposition proceeds. From the rate of decomposition, it appeared as if the water were a 0.1×10^{-7} normal solution of hydroxyl ions, that is, that water is to this extent dissociated under the conditions of experiment. (See next abstract.) J. W.

Electrolytic Dissociation of Water. By W. OSTWALD (*Zeit. physikal. Chem.*, 11, 521—528). From the electromotive force of a gas cell consisting of two electrodes saturated with hydrogen, one immersed in a solution of alkali and the other in a solution of acid, it is possible to calculate the concentration (osmotic pressure) of the hydrogen ions in the alkaline solution, and of the hydroxyl ions in the acid solution. The concentration of these ions in pure water may then be calculated. It follows from the electromotive force actually ascertained (about 0.7 volt) that the concentration of the hydroxyl (and hydrogen ions) in water is 0.9×10^{-6} . (Compare preceding abstract.) J. W.

Electrolytic Dissociation of Acid Salts. By A. A. NOYES (*Zeit. physikal. Chem.*, 11, 495—500).—The author shows that for the acid salt of a weak bibasic acid, H_2A , the following relation holds good:—

$$ck = (k + m)md^2,$$

when k is the dissociation constant of the free acid, c the dissociation constant of the acid ion HA , m the concentration of the salt, and d the ratio of the concentration of the hydrogen ions to m .

Trevor's results (*Zeit. physikal. Chem.*, 10, 32) are found to be in general harmony with this equation. J. W.

The Freezing Points of Sodium Chloride Solutions. By S. U. PICKERING (*Ber.*, 26, 1221—1227).—The author has critically examined, both by the graphic and mathematical methods, the values obtained by Jones (this vol., ii, 263), and finds that they show the presence of the breaks mentioned by him even more clearly than his own results do. Two parabolas deduced from the results so as to recognise the breaks agree perfectly with the ascertained experimental error, whereas a parabola deduced from the same number of points as the preceding ones, but bridging over the breaks, shows an error nearly four times greater than it ought to be, and an attempt to express even one-fourth of the whole of Jones's results as a single curve without any breaks leads to a parabola with an error 10,000 times greater than the experimental error. The author points out that even the most perfect agreement between the freezing point and conductivity results cannot disprove the existence of breaks, or of the

hydrates indicated by them, unless it is first proved that the conductivities are represented by a regular curve. This is far from being the case, and, moreover, the agreement between the two sets of results (even when Jones's values are accepted) is by no means perfect; it is only approximately so as far as a depression of 0.1° . S. U. P.

Freezing Point of very Dilute Solutions. By H. C. JONES (*Zeit. physikal. Chem.*, **11**, 529—551).—In continuation of his former experiments, the author has carefully determined the freezing point of dilute solutions of potassium sulphate, barium chloride, magnesium sulphate, cadmium chloride, cadmium bromide, cadmium iodide, cadmium nitrate, and zinc chloride. The following table shows for potassium sulphate the character of the accordance between the dissociation ratios calculated from the electrical conductivity (Kohlrausch) and from the freezing point:—

	Strength of solution (in equivalents).	Ratio from con- ductivity.	Ratio from freezing point.
K_2SO_4	0.002 normal	92.2 per cent.	94.1 per cent.
„	0.006 „	88.3 „	90.8 „
„	0.01 „	85.8 „	88.2 „
„	0.03 „	78.7 „	82.0 „
„	0.05 „	74.9 „	79.1 „
„	0.1 „	70.1 „	72.0 „

These results indicate that the dissociation ratio of salts may be more correctly ascertained from the electrolytic conductivity (Arrhenius) than from the solubility relations, as Noyes suggests.

J. W.

Dependence of the Solubility of a Solid on its Melting Point. By I. SCHRÖDER (*Zeit. physikal. Chem.*, **11**, 449—465).—For solids which dissolve in liquids without any change in the specific heats occurring, the author has deduced the two following relationships thermodynamically from the theory of osmotic pressure:—

$$\text{I. } \text{Log}_e S = \frac{\rho}{2} \cdot \frac{T_0 - T}{T_0 T}.$$

$$\text{II. } \frac{Q}{T} = \frac{\rho}{T_0} = \text{const.}$$

where S is the ratio of the dissolved molecules to the total number in the solution, ρ the molecular latent heat of fusion of the solid, T_0 its fusion point in the absolute scale, T the temperature at which the solution is saturated, and Q the molecular heat of solution of the solid in its almost saturated solution. Experiments on the solubility of paradibromobenzene in carbon bisulphide, benzene, bromobenzene, and ether, of naphthalene in benzene, chlorobenzene, and carbon tetrachloride, and of metadinitrobenzene in benzene, bromobenzene, and chloroform, gave results in fair accordance with these equations. The alcohols as solvents do not behave as those above mentioned, but are closely similar among themselves. The relationships may be expressed in words as follows: the solubility of different solids in

different liquids is the same when the temperatures are equally removed from the melting points of the solids. J. W.

Participation of a Solvent in Chemical Reactions. By W. NERNST (*Zeit. physikal. Chem.*, **11**, 345—351).—Considerable doubt still exists regarding the question of the nature of the action of a solvent on the soluble substance and in how far this may be considered a chemical action. The author attempts to gain some fresh light in this direction by considering the question from the point of view of the laws of mass action.

If we consider the action between the solvent and soluble substance to be of the kind $A + nB = AB_n$, and if c , c_1 , and c_2 are the concentrations, then, in accordance with the Guldberg-Waage law, $Kc_2 = cc_1^n$. If the solvent B is present in large excess, so that its concentration can only change slightly with an alteration in the conditions of equilibrium, c_1^n may be regarded as constant, that is, the active mass of a solvent at constant temperature is practically constant. If we are dealing with two liquids, and suppose that π is the vapour pressure of the solvent, p that of the dissolved substance, and p_1 that of the solution, then $\pi p = K'p'$. But also $c = kp$ and $c_2 = k'p'$, so that $c_1^n = \pi \frac{K}{K'} \cdot \frac{k'}{k} = \pi \times \text{const.}$ From this it follows that the active mass of a solvent is proportional to its vapour pressure at constant temperature. H. C.

Permeability of Precipitated Membranes. By J. H. MEERBURG (*Zeit. physikal. Chem.*, **11**, 446—448).—The author has repeated some of Tammann's experiments on the permeability of certain precipitated membranes to dyes, choosing those examples which in Tammann's hands gave results contradictory to the "molecular sieve theory" (*Abstr.*, 1892, 1383). The conditions of experiment were so far altered that the dyes were only added to the liquid on one side of the membrane after the membrane itself was completely formed. The results were occasionally irregular, but on the whole were in harmony with the "molecular sieve theory." J. W.

Cyclical Equilibria. By M. WILDERMANN (*Zeit. physikal. Chem.*, **11**, 407—425).—The main object of the present paper was to prove the deduction made by Ostwald from a study of the properties of the factors of chemical energy, that two substances or groups of substances which are each in equilibrium with a third are in equilibrium with one another. A heterogeneous system consisting of two liquids, bromine and water, which are but little soluble the one in the other, was selected, and free acids or salts soluble in the water, but not in the bromine, were afterwards introduced. The bromine dissolves in very different amounts in the different solutions, but the concentration of the vapour above the solutions always remains the same, and equal to that which it shows when water alone is taken. The chemical potential of the common constituent, the bromine, remains the same in all three parts of the different systems, and this may be regarded as proving the deduction above given. H. C.

Laboratory Burner. By N. TECLU (*J. pr. Chem.* [2], **47**, 535—536).—A description of an improvement in the new burner previously described (*Abstr.*, 1892, 768), designed for the simultaneous regulation of the flow of gas and air.

A. G. B.

Light Petroleum Burner. By G. BARTHEL (*Ber.*, **26**, 1179—1180).—The author describes a light petroleum burner consisting of a circular reservoir with two tubes at opposite sides; one is situated at the upper end, and is connected with a small hand bellows, by means of which the petroleum is forced through the second tube, which is at the lower end of the reservoir, and is bent at a right angle; the petroleum is vaporised in the tube, the vapour mixes with air, and is burnt in an ordinary Bunsen's burner. The reservoir is stated not to become unduly heated, and there is no danger of explosion. For a flame 10 cm. high, 40 grams of petroleum per hour are required; for one 20 cm. high, 135 grams. Iron wire, 0.3 mm. in diameter, readily burns with scintillation, and platinum wire, 0.1 mm diameter, quickly fuses.

J. B. T.

Clay Filters. By W. PUKALL (*Ber.*, **26**, 1159—1172).—A description of clay filters made by the Royal Porcelain Manufactory, Berlin. They are made of unglazed, hard-baked clay, so hard that steel will not scratch them, endure a pressure of several atmospheres without breaking, and are attacked, only, and then but to a very slight extent, by hot concentrated sulphuric acid, or caustic soda. They are made in the shape of a flask with flattened bottom, of capacity 50, 135, and 1000 c.c. in the respective sizes, and as cylinders 19 cm. long, of 50 c.c. capacity. These filter at the rate of, roughly, 4900, 8600, 29,600, and 5950 c.c. of pure water per hour respectively, with a difference of pressure of 700—720 mm; the rate is not much less when a turbid mixture is filtered instead of pure water. The filtration is very perfect; from water containing barium sulphate precipitated in the cold, or stannous sulphide, perfectly clear filtrates were obtained, and the complete washing of the precipitate was effected in from three-fifths to two-fifths of the time required with a folded filter. From milk and starch-solution perfectly clear filtrates were also obtained, but these became somewhat turbid on standing. The filter is usually immersed in the liquid to be filtered, and connected, several at once if required, with a large exhaustion-vessel, into which the clear filtrate runs; this vessel is exhausted by means of a water-pump, and then left to itself, a great saving of the water used by the pump is thus effected, as compared with the ordinary method of filter-pump filtration. The filters may be cleaned for further use by rubbing with sand, or, if this is not successful, by dipping in strong acids. If they have been used for filtering oil, for which they are also adapted, they may be cleaned by ignition in a muffle.

C. F. B.

Hygroscopic Properties of Textile Fabrics. By T. SCHLOESING, Jun. (*Compt. rend.*, **116**, 808—812).—The author considers that in determinations of the hygroscopic properties of various compounds

sufficient attention has not been given to the influence of temperature and the coefficient of saturation of the atmosphere. In the case of cotton, wool, merino, and silk, however, the influence of temperature, although distinct, is comparatively small, and this seems to be true also of some other materials. Curves are given showing the relation between the temperatures and the quantity of water absorbed by the textile fabrics specified, when they are allowed to remain for a long time in contact with air having a known coefficient of saturation.

C. H. B.

Inorganic Chemistry.

Hydrogen Peroxide Solutions. By H. P. TALBOT and H. R. MOODY (*J. Anal. Chem.*, **6**, 650—661).—Commercial solutions of hydrogen peroxide were found to contain hydrochloric, sulphuric, phosphoric, and hydrofluosilicic acid, besides sugar, glycerol, barium, calcium, aluminium, and magnesium; in no case was a sample obtained sufficiently pure for direct use in analysis. To purify a commercial solution, it was mixed with 10 per cent. alcohol, and barium hydroxide in powder added to distinctly alkaline reaction, filtered, and the filtrate treated with a slight excess of sulphuric acid; the filtrate, after this treatment, contained 0.003 per cent. of silica, instead of 0.028 originally present. The alcohol was then removed by distillation under diminished pressure. Solutions of hydrogen peroxide may be concentrated by evaporation under diminished pressure; the loss of hydrogen peroxide under a pressure of 30 mm. only amounts to 5 per cent. when the quantity which has distilled over is also taken into account. In this manner solutions of such a concentration were obtained that when unit volumes were mixed with permanganate solution, 588 vols. of oxygen were evolved; whilst the distillates similarly treated evolved 19 vols. of oxygen. When hydrofluosilicic acid is present, it decomposes, and the silicon fluoride evolved reacts with the distillate, forming silicic and hydrofluosilicic acid. The statement that pure hydrogen peroxide solution has an acid reaction is incorrect.

For many purposes, a sufficient purification is effected by neutralising with potash, and allowing the precipitate of silica, potassium silicofluoride, &c., to settle; the supernatant liquid is then decanted through a ribbed filter. About 0.5 per cent. of sulphuric acid should be at once added to the filtered liquid to prevent decomposition.

A. R. L.

Preparation of Perchloric acid. By R. CASPARI (*Zeit. angew. Chem.*, 1893, 68—74).—See this vol., ii, 390.

Decomposition of Gaseous Hydrogen Iodide by Heat. By M. BODENSTEIN and V. MEYER (*Ber.*, **26**, 1146—1159).—Although the course of chemical reactions which take place in solutions has in

many cases been studied with great exactitude, the difficulties in the way of applying accurate measurement to changes taking place in gases are so great, that, up to the present, the only instance in which this has been successfully accomplished is that of the combination of hydrogen with chlorine, in the classical investigation of Bunsen and Roscoe, 36 years ago. To obtain, if possible, some further data with regard to the course of chemical change in gases, the authors have been led to study a reaction which, unlike the one above quoted, is of a reversible character, and in which, therefore, the establishment of a condition of equilibrium will be in no way influenced by such disturbing circumstances as are found to arise in other cases. The reaction selected was the decomposition of hydrogen iodide.

That this reaction is of a reversible nature is, of course, well known, but the authors were surprised to find with what ease combination between hydrogen and iodine takes place, on merely heating the two together, and in the absence of platinum or any other condensing agent. If a sealed tube, filled with hydrogen and containing a little iodine, is heated in sulphur vapour, formation of hydrogen iodide in considerable quantity takes place. The gas is also far more stable than has hitherto been supposed, as a sample of the pure gas was heated for a whole day in the vapour of boiling aniline without being in the least decomposed. Decomposition, at any rate of the pure gas, cannot therefore be said to commence at 180° , as is usually stated. The pure gas is, however, sensitive to the action of light. In bulbs which were exposed for 10 days to the direct action of sunlight, 58 per cent. of the gas was found to have suffered decomposition, and in bulbs freely exposed to sunlight throughout the whole of the summer, 99 per cent. of the gas was decomposed. The decomposition, although slow, is practically complete.

Hydrogen iodide, prepared from phosphorus iodide, cannot, with the utmost care, be completely purified from traces of phosphorus compounds. The gas used in these investigations was therefore prepared by the direct union of hydrogen with iodine in the presence of platinised asbestos. It was passed into water until this was completely saturated, and by gently heating this solution the gas was again obtained. It was then freed from moisture by means of phosphoric anhydride, and from iodine by means of red phosphorus. The gas was passed into glass bulbs provided with lateral capillary tubes, similar to those used by Krause and Meyer, in their investigation on the combustion of gaseous mixtures (Abstr., 1891, 1153). The bulbs had been previously completely freed from air by passing hydrogen through them for 20 hours, with occasional heating to dull redness. When filled with pure hydrogen iodide, the bulbs were sealed, and then submitted to the desired temperature by placing them in the vapour of some liquid of known boiling point. After being allowed to cool, they were opened below the surface of a solution of potassium hydroxide of sp. gr. 1.28, which had been previously boiled to free it from air; in this, hydrogen is practically insoluble. The volume of the gas (hydrogen) remaining unabsorbed showed to what extent the hydrogen iodide had suffered decomposition.

As eventually the direct formation of hydrogen iodide from its

elements under the conditions of the decomposition was also studied, it became necessary to introduce equivalent quantities of hydrogen and iodine into sealed tubes. This, at first sight, difficult operation was effected by taking glass tubes of about 30 c.c. capacity, and introducing into each the necessary quantity of iodine contained in a melting point tube. They were then filled with pure hydrogen, rarefied to $\frac{1}{2}$ atm., and sealed. These tubes were then submitted to a process similar to that above described.

Experiments were first made in the vapour of boiling sulphur (448°), retene (394°), and mercury (350°). As means from several experiments in each case, the following numbers were obtained:—

Temperature of boiling		Relative amount of HI decomposed, determined	
		By decomposition.	By direct union.
Sulphur.....	448°	0·2150	0·2104
Retene.....	394	0·1957	—
Mercury	350	0·1731	0·1738

Decomposition experiments were then made in diphenylamine vapour (310°), and gave as the relative amount of hydrogen iodide decomposed, 0·1669, in place of the expected number of 0·1550, calculated from the above determinations. The difference between the observed and calculated result in this case may be explained on thermodynamical grounds. The heat of formation of hydrogen iodide is at ordinary temperatures negative, but from the fact that the decomposition at high temperatures, 350 — 448° , increases with rising temperature, it follows from Van't Hoff's principle, that the heat of formation at these temperatures is positive. There must, therefore, be a temperature at which the heat of formation is zero, and at which also the decomposition is at a minimum. The point obviously lies between 310° and 350° , and according to a preliminary calculation from the above results is at 324° .

Since the above determinations show that regular conditions of equilibrium were in each case attained, and preliminary experiments rendered it probable that these were only gradually established, attempts were also made to study the decomposition as a time reaction. These proved to be perfectly successful, as it was found that two bulbs heated for the same length of time at the same temperature always gave the same result. The results were calculated by means of the formulæ:—

$$\text{For the decomposition} \dots \frac{dx}{d\theta} = C(1 - x)^2 - C'\left(\frac{x}{2}\right)^2.$$

$$\text{For the combination} \dots \frac{dx}{d\theta} = C'\left(\frac{1 - x}{2}\right)^2 - Cx^2.$$

These by integration gave equations from which the constants C and C' could be calculated. The constancy in the values actually obtained for each of the above temperatures of experiment shows

that in the case of the decomposition of hydrogen iodide by heat the change is one which takes place in a perfectly regular manner.

H. C.

Azoimide from Hydrazine Hydrate and Nitrous acid. By T. CURTIUS (*Ber.*, **26**, 1263).—A dilute solution of azoimide may be conveniently prepared, as a lecture experiment, by passing the nitrous fumes from the action of nitric acid on arsenious anhydride into a cooled, dilute, aqueous solution of hydrazine hydrate until a permanent evolution of gas begins; or, better, by condensing the nitrous fumes on lumps of ice, and adding the blue liquid to the hydrazine hydrate until the evolution of gas begins.

C. F. B.

New Synthesis of Azoimide. By T. CURTIUS (*Ber.*, **26**, 1263—1271).—See this vol., i, 463.

Hyponitrous acid. By C. PAAL (*Ber.*, **26**, 1026—1028; compare W. Wislicenus, this vol., ii, 318).—By the action of silver nitrite on hydroxylamine hydrochloride in aqueous (2 per cent.) solution at 0°, no evolution of gas occurs, and the liquid appears to contain hydroxylamine nitrite; after separation from the silver chloride, the clear solution is treated with silver nitrate and dilute ammonia until no further precipitate is formed; the insoluble portion is washed with water and dissolved in dilute nitric acid; on the addition of ammonia, an additive compound of silver nitrite and silver hyponitrite, $\text{Ag}_2\text{N}_2\text{O}_2 \cdot 2\text{AgNO}_2$, is precipitated; it is deposited from solution in dilute ammonia in small, yellow, granular crystals which readily blacken in the dark.

By the action of nitrous acid on benzylhydroxylamine, benzyl alcohol is formed.

J. B. T.

Constitution of Bleaching Powder. By J. MIJERS (*Zeit. anorg. Chem.*, **3**, 186—192).—A reply to the criticisms of Lunge (this vol., ii, 277) on the author's previous paper on this subject (this vol., ii, 209).

A. G. B.

Formula of Bleaching Powder. By G. LUNGE (*Zeit. anorg. Chem.*, **3**, 351—352).—The author prefers to write $\text{CaOCl}_2 \cdot \text{H}_2\text{O}$, instead of $\text{Ca}(\text{OH})_2\text{Cl}_2$, as the formula of bleaching powder (compare this vol., ii, 209).

J. W.

Silicon. By H. N. WARREN (*Chem. News*, **67**, 136—137).—Aluminium, in pieces the size of a walnut, is introduced into a clay crucible containing a fused mixture of 4 parts of potassium silicofluoride, 1 part of potassium chloride, and 2 parts of potassium carbonate, and when the violent reaction has subsided, the mass is heated to whiteness for five minutes. When cool, the crucible is smashed; the button, carefully detached from adhering slag, is placed in a plumbago crucible with 12 parts by weight of aluminium and 2 of tin, and covered with a layer of sodium silicate; the mixture is submitted for two hours to the strongest heat obtainable. When cold, the piece of aluminium is broken, when the new modifica-

tion of silicon is found in large, lustrous, infusible, oblique octahedrons, insoluble in all acids except hydrofluoric. D. A. L.

Distribution of Calcium and Magnesium in Nature. By N. LUBAVIN (*J. Russ. Chem. Soc.*, **24**, 389—423).—The author discusses the comparative distribution of calcium and magnesium in the animal, vegetable, and mineral kingdoms, using the analytical data that have appeared in the *Jahresbericht* from 1857 to 1886. The solid crust of the earth contains more calcium than magnesium. Meteorites, on the other hand, contain more magnesium than calcium. Magnesium is contained in greater quantity in sea-water, most mineral springs, and in some lakes of Central Asia and Western Siberia; whilst in river water calcium prevails. In general, plants contain more calcium than magnesium, exceptions being found in cereals, some parts of the potato and beet, and in certain maritime plants. Animals also contain calcium in preponderating quantity.

The author has made several series of experiments on the solubility of calcium and magnesium carbonates in water, and in salt solutions, as well as on the double decomposition of the chloride of one metal and the carbonate of the other. The following table contains the solubilities at 26°, expressed in parts of metallic oxide in 100 parts of solution.

	In water.	In 2·525 per cent. solution of NaCl.
Precipitated $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$..	0·0812	0·1250
Magnesite	0·0027	0·0048
Precipitated CaCO_3	0·0005	0·0037
Calcspar	0·0027	0·0053

Calcium carbonate, whether natural or precipitated, is not decomposed appreciably at ordinary temperatures by a solution of magnesium chloride, but magnesium carbonate is completely converted into magnesium chloride by a solution of calcium chloride, the length of time required for the conversion depending on the strength of the calcium chloride solution (compare Bothamley, *Trans.*, 1893, 696).

J. W.

Double Fluorides. By H. v. HELMHOLT (*Zeit. anorg. Chem.*, **3**, 115—152).—The author has prepared double fluorides of ammonium and other metals by dissolving the hydroxide of the metal in ammonium fluoride and evaporating to crystallisation.

Most of the salts which he describes have been prepared before (compare Wagner, *Abstr.*, 1886, 670); the following must now be added to the list:—The *beryllium* salt, $\text{BeF}_2 \cdot 2\text{NH}_4\text{F}$, crystallises in small, colourless needles and prisms; the *cadmium* salt, $\text{CdF}_2 \cdot \text{NH}_4\text{F}$, is a white, crystalline precipitate; the *copper* salt, $\text{CuF}_2 \cdot 2\text{NH}_4\text{F} \cdot 2\text{H}_2\text{O}$, forms blue crystals; the *antimony* salt, $\text{SbF}_3 \cdot 2\text{NH}_4\text{F}$, crystallises in laminæ; the *bismuth* salt, $\text{BiF}_3 \cdot \text{NH}_4\text{F}$, forms transparent crystals. Of these, the copper, bismuth, and cadmium salts are insoluble in water.

The salts $\text{CuF}_2 \cdot \text{KF}$; $\text{CuF}_2 \cdot \text{RbF}$; and $\text{CuF}_2 \cdot \text{NH}_4\text{F} \cdot \frac{1}{2}\text{H}_2\text{O}$ were also prepared.

A. G. B.

Dehydration of Cupric Hydroxide and its Basic Salts. By B. KOSMANN (*Zeit. anorg. Chem.*, 3, 371—376).—The author endeavours to deduce the results obtained by Spring and Lucion (this vol., ii, 210) from thermochemical principles. J. W.

Nitrocopper. By P. SABATIER and J. B. SENDERENS (*Compt. rend.*, 116, 756—758).—Nitrocopper is obtained by passing nitric peroxide at 25—30° over finely divided copper, obtained by the reduction of cupric oxide by means either of hydrogen or of carbonic oxide. Whether prepared with pure nitric peroxide, or with the peroxide diluted with nitrogen, it has the composition Cu_2NO_2 . A small quantity of copper oxide is formed, the proportion increasing with the temperature at which the reaction takes place. Although stable in dry air, the nitrocopper, as previously stated, decomposes into copper and nitric peroxide above 90°, and is violently decomposed by water, with evolution of pure nitric oxide and formation of a solution of copper nitrite and nitrate. Hydrogen has no action in the cold, but if the temperature is rapidly raised to about 180°, ammonium nitrite and free ammonia are formed. Carbonic oxide has no action in the cold, but, on heating, nitric peroxide is given off, and reduced copper is left. Sulphurous anhydride has no special action, but on heating combines with the nitric peroxide that is evolved, and forms the well-known crystalline compound, a residue of partially oxidised copper containing some copper sulphate being left. Chlorine acts in the same way as on reduced copper, copper chlorides being formed, whilst the nitric peroxide is given off. Gaseous ammonia attacks the nitrocopper immediately in the cold, with formation of water vapour and white fumes of ammonium nitrite and nitrate, the mass then suddenly becoming incandescent with formation of large quantities of ammonium salts, whilst a residue containing copper and ammonio-copper oxides, but no copper nitride, is left. Hydrogen sulphide reacts with nitrocopper at the ordinary temperature, with formation of water and sulphur, and, finally, of bright blue cuprous sulphide.

Nitrocopper, in many reactions, behaves as if the copper and the nitric peroxide were intimately associated together, but each retained its own properties. It can therefore be used in many reactions in place of nitric peroxide. C. H. B.

Solubility of Mercuric Iodide in Diiodomethane. By J. W. RETGERS (*Zeit. anorg. Chem.*, 3, 252—253).—Diiodomethane (100 parts by weight) dissolves 2.5 parts of mercuric iodide at 15°, 16.6 parts at 100°, and 58 parts at 180°. On slowly cooling the saturated solution, it deposits large, rhombic plates of the yellow modification, whilst by further cooling, especially in the presence of some of the ready formed substance, quadratic crystals of the red modification are obtained. A. R. L.

Action of Charcoal on Solutions of the Salts of the Rare Earths. By K. HOFMANN and G. KRÜSS (*Zeit. anorg. Chem.*, 3, 89—91).—The neutralised hydrochloric acid solution of the rare earths

was heated on the water-bath with purified animal charcoal, in the expectation that the feebler bases would be precipitated on the surface of the charcoal. This was subsequently incinerated, and the residual oxide was purified by conversion into oxalate. The equivalent of the metal contained in this oxide was $R''' = 155.94$, that of the original having been 138.7.

Animal charcoal cannot be completely freed from phosphate, which vitiates the results. A sugar charcoal was therefore prepared. This, when submitted to the treatment described above, separated an earth which had the equivalent $R''' = 134.4$, that in the original earth having been 116.8. In another experiment, an yttria of $R''' = 93.03$ yielded, by a single treatment with charcoal, an earth giving $R''' = 96$. Such a result could not be achieved by a single precipitation with aniline. The amount precipitated is, however, very small; for instance, 8 grams of charcoal only separated 0.05 gram from 2 grams of earth.

A. G. B.

Behaviour of the Gadolinite Earths with Potassium Chromate. By G. KRÜSS and A. LOOSE (*Zeit. anorg. Chem.*, **3**, 92—107).—The earth used in this investigation was prepared from gadolinite by a preliminary fractionation with ammonia (Abstr., 1891, 1424), followed by a precipitation of the nitrates of the middle fraction with potassium sulphate, and the further fractionation of the earths left in solution by ignition of their nitrates. The fraction submitted to treatment with potassium chromate had an equivalent of $R''' = 102$. A solution of the nitrate was mixed with potash until there was a slight precipitate, which was filtered off. Potassium chromate was added and the mixture warmed as long as the precipitate increased; the solution became red from the production of potassium dichromate. The precipitated chromate was dissolved in hydrochloric acid, reduced by alcohol, nearly neutralised by ammonia, and precipitated as oxalate. The filtrate from the chromate was again treated as described above; three such fractions were prepared. The first, contrary to expectation, gave a brown oxide, showing the presence of much didymium, the strongest of these bases; it had the equivalent $R''' = 115.6$; the second and third fraction gave lighter oxides and had the equivalents $R''' = 111$ and 104.3 respectively. Spectroscopic examination of the three fractions showed that the first was rich in didymium and erbium, which are respectively the strongest and weakest of these bases, whilst yttria appeared in the following fractions. It thus seemed probable that didymium was thrown down as chromate, and the erbium as basic chromate or free base, accounting for the production of potassium dichromate.

Further experiments showed that an approximate separation of didymium could be effected by precipitation with potassium chromate in a cooled solution, leaving the erbium to be precipitated on heating, together with more didymium, as basic chromates.

A preparation of didymium oxide, obtained by repeated precipitation with potassium chromate in the cold until the erbium lines disappeared from the spectrum, gave an equivalent $R''' = 145.3$, a result probably too high, but explicable in part by the fact that it

contained excess of oxygen, indicated by its brown colour. A heating in hydrogen showed that 0.5 per cent. oxygen had been absorbed in excess. The precipitate was proved to be a didymium chromate, and not a double potassium salt.

A. G. B.

Action of Aniline and Aniline Hydrochloride on the Gadolinite Earths. By G. KRÜSS (*Zeit. anorg. Chem.*, **3**, 108—114).—The fractionation of these earths by aniline has been already dealt with (Abstr., 1891, 1425). If the bases can be fractionally displaced from their chlorides by aniline, it follows that the hydroxides must be fractionally soluble in aniline hydrochloride. The best method of applying this principle is to acidify the solution of the chlorides of the earths with hydrochloric acid, to add a quantity of aniline about equivalent to the earths in solution, and then ammonia equivalent to the quantity of earth which it is desired to precipitate; after warming for $1\frac{1}{2}$ hours at 80° , the precipitate is filtered off through a dry filter. If it be required to separate the feeble bases from the stronger, only a little ammonia is added, so that the precipitate may contain only the feeblest bases; if, on the other hand, the strongest bases are required, much ammonia is added, so as to leave these only in solution. The author designates the former process "aniline precipitation," and the latter "aniline solution." The method will be further developed.

A. G. B.

Erbia. By G. KRÜSS (*Zeit. anorg. Chem.*, **3**, 353—369).—If ytterbium earths containing erbium are submitted to fractionation by decomposition of the nitrates by heat, or by the action of aniline or aniline hydrochloride, and if those fractions are considered as erbium earths which have an equivalent $\text{Er}''' = 166$ —168 and show the absorption lines $\lambda = 654.7$ and $\lambda_1 = 523.1$, then an apparently homogeneous oxide is obtained, with the properties ascribed by Cleve to erbia. The same result is reached if fractional decomposition of the nitrates by heat alone is pursued far enough. When, however, apparently all the ytterbium, holmium, terbium, and yttrium have been removed by the above methods, and an erbium with a constant equivalent has been obtained, it is possible, by fractionation with aniline hydrochloride, to decompose the earth further into substances with different equivalents. Erbium is therefore not a homogeneous earth, but consists of several substances, further researches on which are promised by the author.

J. W.

Behaviour of Aluminium towards Mercuric Salts. By J. KLAUDY (*Chem. Centr.*, **i**, 1893, 201; from *Rep. Pharm.*, **3**, 89).—When aluminium is brought into an aqueous solution of mercuric chloride, aluminium amalgam is first formed, and subsequently it is decomposed by the water, the aluminium being converted into chloride. When aluminium is added to a concentrated alcoholic solution of mercuric chloride, a very energetic reaction ensues; mercury is first deposited on the aluminium, which latter slowly dissolves. When the mixture is warmed, the reaction becomes violent enough to cause the alcohol to boil, and when the reaction is complete, a small quantity of gas, probably hydrogen, is evolved. Ethylic chloride was not detected.

Towards the end of the reaction only is the alcohol decomposed, whilst the excess of aluminium dissolves as basic chloride. The amalgam produced at the first stage contained 1 part of mercury and 36.1 parts of aluminium. Other mercuric salts behave in the same manner as the chloride, and the amalgam is formed when chloroform or aldehyde is used as solvent. The amalgam has a great affinity for oxygen; it quickly becomes heated to 80° on exposure to the air, decomposes water, reduces potassium dichromate, permanganate, ferricyanide, indigo, nitrobenzene (in alkaline solution), and precipitates electropositive metals from their solutions. It dissolves readily in acids and alkalis, does not decompose absolute alcohol, decomposes dilute alcohol only to a slight extent, and is indifferent towards hydrocarbons.

A. R. L.

Volatility of Manganese at High Temperatures. By R. LORENZ and F. HEUSLER (*Zeit. anorg. Chem.*, 3, 225—229).—The authors confirm the observations of Guntz concerning the non-existence of a manganese carbonyl at temperatures comparable with those at which ferrocabonyl and nickel carbonyl are formed (Abstr., 1892, 568). When manganese carbide, Mn_3C , was heated to whiteness in a current of carbonic oxide, the metal was melted and the walls of the tube were covered with finely-divided manganese. But this was not due to the formation of a manganese carbonyl, for the same result was obtained when hydrogen or nitrogen was substituted for carbonic oxide. No absorption of the nitrogen by the metal was observed. The authors conclude that manganese is volatile at a temperature a little above its melting point (compare Jordan, Abstr., 1878, 772).

A. G. B.

Iron Chlorobromide. By C. LENORMAND (*Compt. rend.*, 116, 820—823).—Bromine acts very slowly on anhydrous ferrous chloride at the ordinary temperature, combination being incomplete even after a month. In sealed tubes at about 100° , the result varies with the proportion of bromine employed. If the chloride and the bromine are mixed in the proportions $2FeCl_2 : Br_2$, combination takes place, but no crystals are formed; if, however, the bromine is in excess, *ferric chlorobromide*, $Fe_2Cl_4Br_2$, separates in volatile crystals which are insoluble in excess of bromine. The crystals are lustrous, and very dark coloured, green by reflected light, and completely opaque even in thin sections. They seem to be hexagonal tables. The compound is very deliquescent, and very soluble in water; it also dissolves readily in alcohol or ether, and, by means of the latter, can be separated from ferrous chloride. Chloroform, benzene, and toluene also dissolve it, but carbon bisulphide dissolves only a trace. It is easily decomposed by heating, but sublimes readily when heated in a tube containing a slight excess of bromine.

When bromine is added to ferrous chloride solution, combination takes place with considerable development of heat, and, after expulsion of the excess of bromine, the composition of the liquid agrees with the formula $Fe_2Cl_4Br_2$. The solution is very deep red when concentrated, and yellow when dilute. It has an acid reaction, and contains colloidal ferric oxide.

C. H. B.

History of Complex Inorganic Acids. By C. FRIEDHEIM (*Zeit. anorg. Chem.*, **3**, 254—263).—The author replies to certain remarks made by Kehrman (*Zeit. anorg. Chem.*, **3**, 76) on his previous paper (*Abstr.*, 1893, ii, 282). Finkener must be regarded as the discoverer of this class of compounds. A. R. L.

Complex Inorganic Acids. By F. KEHRMANN (*Zeit. anorg. Chem.*, **3**, 377—379).—A rejoinder to Friedheim.

Preparation and Specific Gravity of Uranium Dioxide. By W. F. HILLEBRAND (*Zeit. anorg. Chem.*, **3**, 243—248).—Wöhler obtained uranium dioxide by evaporating a solution of uranium oxychloride, UO_2Cl_2 , with an excess of sodium and ammonium chloride, and fusing the residue. Uhrlaub (1861) stated that the product was a nitrogenous compound of the formula $\text{U}_{10}\text{N}_4\text{O}_{18}$. The author finds that when air is completely excluded during the fusion, an almost qualitative yield of uranium dioxide is obtained, and that Uhrlaub's compound does not exist or, at any rate, is not obtainable under the conditions mentioned. The specific gravity of crystallised uranium dioxide (reduced to a vacuum and compared with water at 4°) is certainly not lower than 10.95, and is probably 11. A. R. L.

Further Example of the Isomorphism of Thorium and Uranium Dioxides. By W. F. HILLEBRAND (*Zeit. anorg. Chem.*, **3**, 249—251).—When an oxide of uranium is fused with borax for 24 hours, and the cold mass extracted with water and dilute acetic or hydrochloric acid, jet-black octahedra of uranium dioxide are obtained. The appearance of the crystals is unaltered when thorium dioxide is one of the constituents of the mixture, as the latter is isomorphous with uranium dioxide. A. R. L.

Solubility of Metallic Iodides, &c., in Methylenic Iodide. By J. W. RETGERS (*Zeit. anorg. Chem.*, **3**, 343—350).—100 parts of methylenic iodide dissolve 22.9 parts of stannic iodide at 10° , the sp. gr. of the solution at that temperature being 3.481. The solubility increases rapidly with rise of temperature, the stannic iodide separating on cooling as highly refractive octahedra, with or without cubic faces. Arsenious iodide also dissolves in methylenic iodide to the extent of 17.4 parts in 100 of solvent. The solution is dark red, and has the sp. gr. 3.449 at 12° , the temperature of experiment. 100 parts of methylenic iodide dissolve 11.3 parts of antimonious iodide at 12° , giving a solution of sp. gr. 3.453. Bismuth iodide is much less soluble, only 0.15 part dissolving in 100 of the solvent at 12° . The solubility is scarcely affected by a rise of temperature.

Lead iodide, cadmium iodide, ferrous iodide, thallic iodide, mercurous iodide, cuprous iodide, and silver iodide are only dissolved in traces, if at all, by methylenic iodide. The boiling solvent does not dissolve the double compound $2\text{TiI}_2\cdot\text{HgI}_2$, but partially decomposes it into its constituents.

10 parts of powdered sulphur dissolved in 100 parts of methylenic iodide at 10° . Melted sulphur mixes freely in all proportions with

methylenic iodide. 100 parts of the same solvent dissolve 1·3 parts of selenium, and 0·1 part of tellurium at 12°. Iodine is very soluble in methylenic iodide, and so likewise is yellow phosphorus, red phosphorus being quite insoluble. Neither arsenic nor antimony could be appreciably dissolved. J. W.

Specific Gravity of Titanium. By K. B. HOFMANN (*Ber.*, 26, 1025—1026).—The titanium employed was obtained as a fine powder by the action of sodium vapour on potassium titanium fluoride in an atmosphere of hydrogen. Two series of determinations made with 1·977 grams and 1·5944 grams of the metal, and calculated, according to Kohlrausch's formula, gave the sp. gr. = 3·4973 and 3·5888 respectively, of which the author believes the latter to be the more correct value. The atomic volume = 13·4. J. B. T.

Formation of Thiovanadates. By G. KRÜSS (*Zeit. anorg. Chem.*, 3, 264—266; compare Abstr., 1890, 1381; 1891, 989).—By fusing together vanadic oxide, soda, and sulphur until the excess of the latter is driven off, the anhydrous salt $\text{Na}_3\text{VS}_3\text{O}$ (*loc. cit.*) is obtained. A similar result was obtained by Norblad (*Upsala Univers. Arsskrift*, 1874). Potassium and ammonium salts cannot be obtained by the dry method as they undergo decomposition. A. R. L.

Constitution of Inorganic Compounds. By A. WERNER (*Zeit. anorg. Chem.*, 3, 267—330).—A theoretical paper devoted to the discussion of the so-called ammonio-metallic compounds. The formula of "platinosodiamine chloride" may be written $\text{Pt}(\text{NH}_3\cdot\text{NH}_2\text{Cl})_2$ or $\text{Pt}(\text{NH}_2\text{Cl}\cdot\text{NH}_3)_2$. Jörgensen's observation that tertiary amines, as well as pyridine, form compounds analogous to these, favours the first formula, because although it is conceivable that two residues of ammonia may combine thus: $\text{=NH}_2\cdot\text{NH}_3$, this cannot be the case with a tertiary amine in which the whole of the hydrogen is replaced by alkyl groups. A. R. L.

Composition of the Precipitate obtained with Hydrogen Sulphide in Solutions of Potassium Iridiochloride. By U. ANTONY (*Gazzetta* 23, i, 184—190).—Berzelius and Fehling (*Fehling's Handwörterbuch*, 3, 812) state that iridium bisulphide is obtained by the action of hydrogen sulphide on solutions of iridic chloride or potassium iridiochloride; contradictory observations are, however, recorded by Claus (*Gmelin-Kraut, Handbuch*, 3, 1311). The author has, therefore, again investigated the action of hydrogen sulphide on solutions of potassium iridiochloride. Pure iridium, prepared by the author's method (Abstr., 1892, 1285), was mixed with potassium chloride, and heated at 300° in a stream of chlorine; the iridiochloride was then extracted with boiling water and crystallised. On passing hydrogen sulphide through a 2 per cent. aqueous solution of the salt at 90—100°, a brown precipitate separated, and the solution gradually lost its dark colour, but, even after prolonged passage of the gas, it still remained reddish-yellow; the precipitate was collected, washed with hydrogen sulphide solution, avoiding contact with the

air, and dried at 90° in a stream of carbonic anhydride. The powder thus obtained underwent no alteration in the air and contained no free sulphur; it was analysed by roasting it to metal in a stream of air, and gave results which in the author's opinion show it to be a mixture of iridium bisulphide and sesquisulphide approximating in composition to $2\text{IrS}_2, \text{Ir}_2\text{S}_3$. This view is also supported by the persistent colour of the solution from which the sulphide was precipitated, the sesquisulphide being slightly soluble in water. The chlorine, which would be liberated if iridium sesquisulphide were formed, should oxidise the hydrogen sulphide to sulphuric acid, and accordingly sulphuric acid was found in the solution. If the treatment with hydrogen sulphide takes place at $20\text{--}30^{\circ}$, a smaller proportion of sesquisulphide is formed, the precipitate approximating in composition to $6\text{IrS}_2, \text{Ir}_2\text{S}_3$; at 0° a still larger proportion of the bisulphide is present in the precipitate.

The observations of the older workers on this subject are hence erroneous. W. J. P.

Lithium Iridiochloride and Iridium Bisulphide. By U. ANTONY (*Gazzetta*, 23, i, 190—194).—*Lithium iridiochloride* may be prepared by passing dry chlorine over a mixture of iridium with carefully dehydrated lithium chloride at 300° ; the salt is then extracted with water and crystallised. It is thus obtained in minute, garnet-red needles, which are somewhat deliquescent; on drying at $90\text{--}100^{\circ}$ in a current of air, it forms a dark red powder.

The author has shown (see preceding abstract) that the precipitate formed by hydrogen sulphide in iridium solutions is a mixture of iridium bisulphide and sesquisulphide; it is hence impossible to obtain the bisulphide by the wet method. It may, however, be prepared by passing hydrogen sulphide over lithium iridiochloride at $4\text{--}7^{\circ}$; no action occurs below 0° , and at above 10° the salt is very rapidly attacked with formation of free sulphur. On repeatedly extracting the mass with absolute alcohol and drying the residue at $90\text{--}100^{\circ}$ in a current of carbonic anhydride, *iridium bisulphide*, IrS_2 , is obtained as a brown powder, which is not affected by exposure to moist air. It is partially decomposed by water with separation of sulphur, and when heated at 300° in the air it gives metallic iridium; it is not attacked by hydrochloric acid or ordinary nitric acid, but is readily decomposed by fuming nitric or nitrohydrochloric acid. On heating at a low red heat in a current of carbonic anhydride, it loses sulphur, as already stated by Berzelius, yielding iridious sulphide.

W. J. P.

Osmium. By H. MORAHT and C. WISCHIN (*Zeit. anorg. Chem.*, 3, 153—179).—The black osmium oxide, originally obtained by Eichler by the action of nitric acid on potassium osmate, and supposed by him to be $\text{K}_2\text{O}, 3\text{OsO}_2$, was afterwards obtained by Fremy, and again by Claus and Jacoby, by exposing a solution of potassium osmate to sunlight; the latter chemists assigned to it the formula $\text{OsO}_2, 2\text{H}_2\text{O}$.

The authors have reinvestigated this substance, dried over phosphoric anhydride in a vacuum until constant in weight, and find that

it is osmic acid, H_2OsO_4 . It was analysed in several ways with concordant results; the methods are described in the paper.

Osmic acid is sooty-black, and when dry does not possess any of the coppery lustre alleged by Claus and Jacoby to be characteristic of $\text{OsO}_2 \cdot 2\text{H}_2\text{O}$. In moist air, it has a strong odour of perosmic anhydride, but is stable under water which contains alcohol. It dissolves in nitric acid to perosmic anhydride, and in boiling hydrochloric acid to an olive-green solution which smells of chlorine. It is not attacked by sulphuric acid.

When hydrogen sulphide is passed over osmic acid, a violent reaction occurs, much heat is evolved, and osmium oxysulphide, $\text{Os}_2\text{S}_2\text{O}_2 \cdot \text{H}_2\text{O}$, is formed. This is a brown powder, which is decomposed and dissolved by nitric, hydrochloric, and sulphuric acids (compare E. v. Meyer, *Abstr.*, 1878, 14). Considering the high temperature which accompanies the formation of this compound, the authors are of the opinion that the hydrogen must be present in the form of OH or SH, and quote some evidence in support of the formula $\text{O}(\text{OsO} \cdot \text{SH})_2$. By further heating in hydrogen sulphide, it is converted into OsS_2 .

Osmic acid was heated with strong hydrochloric acid in a reflux apparatus for 48 hours, a little alcohol being added to hinder the formation of perosmic anhydride; chlorine was evolved, and a slight, black residue left undissolved; after filtering and evaporating in a vacuum, large, well-formed, six-sided pyramids of the chloride $\text{Os}_2\text{Cl}_7 \cdot 7\text{H}_2\text{O}$ were obtained. In moist air this salt is dark, olive-green, but when absolutely dry it is the colour of minium; it dissolves in alcohol and water with a dark green colour and crystallises again unchanged. It would appear, however, that this chloride is a mixture of OsCl_4 and OsCl_3 ; for when its alcoholic solution is mixed with a solution of potassium chloride, potassium osmium chloride, K_2OsCl_6 , separates in the form of red octahedra, and if the filtrate from this be evaporated in a vacuum, a crystalline residue of $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ is left.

Osmium is not attacked by bromine vapour. When osmic acid is treated with hydrobromic acid, in the manner described above for hydrochloric acid, small, dark brown, prismatic crystals having the composition $\text{Os}_2\text{Br}_9 \cdot 6\text{H}_2\text{O}$ are isolated. This compound appears to be made up of OsBr_3 and OsBr_6 , and is being further investigated. Indications of the existence of an oxybromide were obtained.

There is no reaction between osmium and iodine vapour, nor between osmic acid and iodine vapour. The iodide obtained by heating osmic acid with hydriodic acid was difficult to analyse, but appeared to be OsI_4 . It forms violet-black crystals which appear to be rhombohedra, and have a metallic lustre; it dissolves to a red-brown solution in alcohol and in water, and when the solution in aqueous alcohol is heated, a black powder is deposited which has a coppery lustre when dry, and appears to be an oxyiodide.

The existence of an osmium oxyfluoride was proved.

A. G. B.

Mineralogical Chemistry.

Sundite, a new Mineral from Oruro, in Bolivia. By C. BRÖGGER (*Zeit. Kryst. Min.*, **21**, 193—199).—In a collection of Bolivian minerals presented to the Christiania University by L. Sundt, there is a series of specimens of a new silver ore. The mineral, which resembles tetrahedrite in appearance, crystallises in the rhombic system. It is very brittle, and has a hardness of 3 to 4, and a sp. gr. of 5.5. Analysis yielded the following results:—

Cu.	Ag.	Fe.	Sb.	S.	Total.
1.49	11.81	6.58	45.03	35.89	100.80

The formula is probably $(\text{Ag}_2\text{Cu}_2\text{Fe})\text{S}_3\text{Sb}_2\text{S}_3$.

Sulphantimonates of similar composition have not hitherto been met with in nature.

B. H. B.

Melanostibian, a new Swedish Mineral. By L. J. IGELSTRÖM (*Zeit. Kryst. Min.*, **21**, 246—248).—At the celebrated Sjö manganese mine, in the Government of Orebro, where numerous rare minerals have been discovered, a new antimony mineral has been found occurring in veins 1 to 2 cm. in width in dolomite. This has been named *melanostibian* by the author, from μέλας (black) and the Latin *stibium* (antimony). The mineral is black, its powder being cherry-red. Its hardness is 4. Analysis gave the following results:—

Sb_2O_3 .	FeO.	MnO.	CaO.	MgO.	H_2O .	Total.
37.50	27.30	29.62	1.97	1.03	1.06	98.48

Its formula is $6(\text{MnFe})\text{O}, \text{Sb}_2\text{O}_3$.

B. H. B.

Melanophlogite. By E. MALLARD and G. FRIEDEL (*Bull. soc. fran. min.*, **13**, 180 and 356).—In an exhaustive description of this mineral from the Solfatara Giona at Racalmuto, an analysis is given of absolutely pure melanophlogite, the results being as follows:—

SiO_2 .	SO_3 .	Fe_2O_3 .	
93.18	6.19	0.29	B. H. B.

Titaniferous Iron Ore from the Breitfirst. By R. WEDEL (*Zeit. Kryst. Min.*, **21**, 259).—In a description of the dolerite district of the Breitfirst, a range of hills extending from the Rhone to the Spessart, the author gives analyses of plagioclase, augite, and titaniferous iron ore from the doleritic plagioclase-basalt of the district. Analysis of the titaniferous iron ore from the unweathered (1) and the weathered (2) rock gave the following results:—

	TiO_2 .	Fe_2O_3 .	FeO.	MgO.	Total.	Sp. gr.
I.	45.03	11.18	42.59	1.89	100.69	4.68
II.	47.08	13.06	39.97	0.84	100.95	4.69

B. H. B.

Physiological Chemistry.

Influence of dividing the Daily Nutriment on the Metabolism of the Dog. By C. ADRIAN (*Zeit. physiol. Chem.*, 17, 616—633).—Full details are given of the metabolic exchanges in a dog fed, first, on a given amount of flesh, and secondly, on the same amount divided into four portions in the course of the day. In the latter case, there was an increase in body weight, in nitrogen output, and in output of urea. An increased absorption of proteid takes place if the four meals are given instead of one. Under such circumstances, the amount of loss by the fæces is diminished, and also less proteid is broken up by pancreatic and bacterial action into simple products which are of little use to the organism.

The application of this to the dieting of human individuals is obvious. W. D. H.

Sugar in Muscle. By A. PANORMOFF (*Zeit. physiol. Chem.*, 17, 596—606).—The amount of sugar in muscle is very small in warm-blooded animals, from 0·01 to 0·03 per cent. It does not come from the blood in the muscles, as muscles freed from blood yield about the same quantity. The sugar is dextrose, identified by the phenyl-glucosazone which was made from it. There is no evidence of maltose in muscles, as Pavy (*Lancet*, 1881, ii, 5 and 43) has stated. The glycogen in muscles disappears after death, but there is no corresponding rise in sugar; probably it forms lactic acid.

W. D. H.

Goat's Milk. By SCHAFER (*Chem. Centr.*, 1893, i, 620—621; from *Schweiz. Woch. Pharm.*, 31, 58—60).—See this vol., ii, 396.

The Acids of Ox Bile. By LASSAR-COHN (*Zeit. physiol. Chem.*, 17, 607—615; compare *Abstr.*, 1892, 1114, 1503).—Further investigations have not led to the identification of any further acids in ox bile. The methods described, employed on large quantities of ox bile, have led to the following quantitative results. The acids given below are those organic acids which are precipitated by hydrochloric acid after boiling with sodium hydroxide. There is a total percentage of 5·195, made up as follows:—

Cholic acid.....	4·790
Choleic acid	0·085
Stearic acid.....	}
Palmitic acid	
Oleic acid	
Myristic acid.....	0·004
Resinous acids	0·120
	5·145
Loss	0·050

W. D. H.

Uric acid in the Organism. By C. WULFF (*Zeit. physiol. Chem.*, 17, 634—643).—The experiments of Horbaczewski (*Abstr.*, 1892, 646) are not conclusive, as the uric acid he obtained must have been contaminated with xanthine. A method is described for the quantitative separation of these two substances, which depends on the fact that dilute hot nitric acid breaks up uric acid into higher oxidation products, whilst xanthine is not affected. W. D. H.

Action of Nitrites on Muscular Tissue. By J. T. CASH and W. R. DUNSTAN (*Proc. Roy. Soc.*, 52, 91—93).—Experiments on skeletal muscles of the frog were conducted in an air-tight chamber, so constructed as to permit of connection being made between the muscle and recording apparatus, and also so that the vapour of a known quantity of nitrite could be introduced. The nitrites produce shortening; their order of activity in relation to the extent of this shortening is (1) isobutylic, (2) tertiary amylic, (3) secondary butylic, (4) secondary propylic, (5) propylic, (6) tertiary butylic, (7) butylic, (8) α -amylic, (9) β -amylic, (10) ethylic, (11) methylic. The order representing the speed with which shortening occurs is (1) methylic, (2) ethylic, (3) secondary propylic, (4) tertiary amylic, (5) primary propylic, (6) tertiary butylic, (7) secondary butylic, (8) α -amylic, (9) β -amylic, (10) primary butylic, (11) isobutylic.

In minute doses, insufficient to cause passive contraction, nitrites lessen the irritability of muscle.

This physiological action is not solely, and in some cases not even mainly, dependent on the amount of nitroxyl (NO_2) they contain. In all phases of physiological activity, the secondary and tertiary are more powerful than the corresponding primary compounds; this is due to the great facility with which they are decomposed into the alcohol and nitrous acid. In accelerating the pulse, the power of the nitrites is directly as their molecular weight, and inversely as the amount of nitroxyl they contain. The same relationship holds, although less uniformly, in their power of reducing blood pressure and inducing muscular contraction. This appears to be due to the increased chemical instability which the substituted methyl groups confer on the higher members of the series. The reverse order holds for the most part in relation to the duration of subnormal pressure, and the rapidity of the onset of muscular contraction. The simpler nitrites probably attach themselves to certain constituents of blood and muscle, and thus act more quickly than the higher compounds, whilst their greater stability causes their effect to last longer.

A large proportion of organic nitrite is changed into nitrate in its passage through the organism, and is excreted in the urine as an alkali nitrate. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Are Nitrates Indispensable for the Growth of Plants? By O. PITSCH (*Landw. Versuchs-Stat.*, 42, 1—95; compare Abstr., 1888, 84).—The paper gives the results of experiments made from 1886 to 1891. The plants were grown in poor sandy soil, containing about 0.11 per cent. of nitrogen, and supplied in each case with the necessary mineral constituents, without nitrogen, with nitrogen as nitrate, and with nitrogen as ammonia. In each set of experiments, the ammonia was applied as sulphate, and in some cases, also, as phosphate. The plants employed were barley, wheat, oats, beetroot, and beans. The soils were sterilised as already described (*loc. cit.*). In 1888, an alteration was made in the apparatus, so that water could be applied at the surface of the soil. The following table gives the results of all the experiments (except those with ammonium phosphate, which do not differ materially from those in which the sulphate was employed), and shows the amount of nitrogen applied and the amount of dry produce.

The growth was normal in each case, but was generally much less where there was no nitrate than when nitrate was given. The pots which had no application of nitrogen gave generally as much growth as those supplied with ammonia. Different plants seem to behave

	Ammonium sulphate.	Sodium nitrate.	Soil.	
			Sterilised and extracted.	Not sterilised and extracted.

Barley grown in (1) 1886–87, (2) 1888, and (3) 1890.

1 {	Total N applied....	0.595	0.773	0.862	—	(0.78)
	Dry produce	39.8	63.8	63.8	—	64.9
2 {	Total N applied....	0.515	0.347	0.703	0.463	—
	Dry produce	17.9	24.5	37.2	34.0	20.0
3 {	Total N applied....	0.8143	0.8523	0.8284	0.8347	—
	Dry produce	48.2	(12.5)*	100.9	(34.9)*	57.6 (10.2)*

Wheat grown in 1886–87.

Total N applied.....	0.557	0.56	0.56	—	(0.557)
Dry produce.....	58.1	70.0	61.9	—	70.6

* These plants were cut at an early period of growth.

	Ammonium sulphate.	Sodium nitrate.	Soil.	
			Sterilised and ex-tracted.	Not sterilised and ex-tracted.

Oats grown in (1) 1889, (2) 1890, and (3) 1891.

1 {	Total N applied....	0·876	0·435	0·8827	0·4315	—	—
	Dry produce	23·7	20·7	74·1	66·7	24·7	65·2
2 {	Total N applied....	0·652	0·649	0·651	0·649	—	—
	Dry produce	13·4	15·8	82·0	75·9	{ 20·1 14·5 }	—
3 {	Total N applied....	0·810	0·409	0·810	0·409	—	—
	Dry produce	17·8	28·5	77·1	55·1	36·7*	—
						13·0	

Beetroot grown in (1) 1887, (2) 1888, (3) 1889, and (4) 1891.

1 {	Total N applied....	0·439		0·434		—	—
	Fresh produce	159·4		169·9		—	—
2 {	Total N applied....	0·788	1·712	0·822	1·643	—	—
	Dry produce	79·7	92·4	83·9	142·3	—	137·1
3 {	Total N applied....	2·200	1·169	2·356	1·136	—	—
	Dry produce	48·3	53·8	181·6	119·6	33·6	—
4 {	Total N applied....	2·241	2·241	2·241		—	—
	Dry produce	55·9	74·8	117·7		66·8	—

Beans grown in 1887.

N per kilo. of soil	0·0118	0·0116	—	—
Dry produce.....	27·2	41·2	—	—

* Top dressing contains 0·135 gram of nitrogen.

differently towards ammonia; in the case of oats, the difference between the nitrate and ammonia plants was always very considerable. The plants grew in sterilised soil as well as in soil not sterilised, when both soils contained nitrogen in the same form. Beans, when grown in soils which had been heated at 100°, behaved like barley; they were able to develop when supplied with ammonia, but were much stronger when grown in presence of nitrate. With the single exception of winter wheat, all the plants were much more benefited by nitrate than by ammonia, the difference being shown not only by the production of a heavier crop but more especially in the earlier stages of growth, when the presence of nitrate seems to be

most necessary. The presence of nitrate in the soil seems to enable the plant to take up more nitrogen in other forms (ammonia?) than when the soil was left unmanured or was supplied with ammonia. In every case (except wheat) the nitrate plant utilised much more of the nitrogen of the soil present in other forms than nitrate (ammonia?) than the ammonia plants did. The more favourable action of nitrate was evident in every stage of development of the plants, and the plants so manured were always the first to ripen.

The young plants seemed particularly sensitive towards ammonia, the corn plants losing early the points of the first leaves, whilst the leaves of the beetroot plants showed brown spots and died earlier than those which received nitrate. This difference was especially noticeable when the young plants were exposed to the sun.

There is evidence that, in the course of the experiments, nitrification did not take place in the sterilised pots, and that nitrifying bacteria do not occur in the air.

N. H. M.

Analytical Chemistry.

Electrometric Analysis. By R. BEHREND (*Zeit. physikal. Chem.*, 11, 466—491).—The author proposes to use a sensitive electrometer as an indicator in volumetric analysis as follows: If, for example, a two-fluid cell is constructed, having for electrodes mercury, and for liquids solutions of mercurous nitrate and potassium chloride, then a large electromotive force will be observed between the poles. If, now, a solution of mercurous nitrate is added from a burette to the solution of potassium chloride, the electromotive force sinks at first slowly, but with slightly increasing velocity as more mercurous nitrate enters the liquid, until at the point when all the halogen present has been precipitated by the mercurous salt, it suddenly falls to a value not far removed from zero. The point at which the sudden fall takes place indicates when equivalent quantities of the reagents are present. Thus, in the above case, the amount of halogen in the potassium chloride solution may be estimated by titration with mercurous nitrate. The author has made corresponding experiments with silver salts and silver electrodes, and finds that, by using ammoniacal solutions, he can not only estimate the total halogens in the mixture but the amount of iodine separately.

J. W.

Use of Sodium Peroxide in Analysis. By W. HEMPEL (*Zeit. anorg. Chem.*, 3, 193—194).—The author points out that this compound can now be obtained free from sulphur, nearly free from chlorine, and containing some 60—70 per cent. of sodium peroxide, the rest being sodium oxide. For the usual method of detecting chromium and manganese it is admirable, and is much to be recommended for decomposing tungsten minerals and titaniferous iron ores. It serves excellently for attacking sulphides whose sulphur is to be determined, only for this

purpose it must be diluted with half its weight of soda, otherwise the reaction is explosively violent; 1 part of the mineral to 2 parts of soda and 4 parts of sodium peroxide is recommended. The heating is conducted in a silver crucible, and the reaction is over in a few minutes. The mass is dissolved in water, any ferric oxide filtered off, and the sulphuric acid determined as usual. Results are quoted to show the concord between the results obtained by such a method and those obtained by solution in aqua regia.

A. G. B.

Estimation of Chlorides, Hypochlorites, and Chlorates in presence of each other. By M. ROSENBAUM (*Zeit. angew. Chem.*, 1893, 80).—*Estimation of Calcium Chloride in Bleaching Powder.*—An aliquot part of the original solution is boiled to destroy the hypochlorite, and the solution is afterwards titrated with silver nitrate using potassium chromate as indicator. (Allowance should, of course, be made for the chloride formed by the decomposition of the hypochlorite.)
—ABTRACTOR.)

Estimation of Calcium Chlorate.—An aliquot part of the solution is boiled for some time, then cooled and mixed with a definite quantity of ferrous ammonium sulphate and an excess of sulphuric acid. The mixture is now boiled, again cooled, and the excess of iron is then titrated back with permanganate. The amount of chlorate is easily found by calculation. (Allowance must, of course, be made for the chlorate produced from the hypochlorite.)

Estimation of Calcium Hypochlorite.—This estimation, on which, of course, the accuracy of the other determinations depends, is done by Pennot's process by means of arsenious acid and iodine solution. Free chlorine is also occasionally present in samples of bleaching powder, but the author states that the amount is so small that its estimation may be safely neglected.

L. DE K.

Estimation of Oxygen in Iron. By P. GLADKY (*Chem. Centr.*, 1893, i, 440—441; from *Russ. Berg. J.*, 2, 81—83).—In the estimation of oxygen in iron by heating the metal in a current of hydrogen and weighing the water produced, errors may accrue from the absorption of oxygen during the filing or boring to obtain the sample. A sample of iron containing 0.65 per cent. of carbon gave on analysis 0.082 per cent. of oxygen, which latter amount is improbable, taking into account the high percentage of carbon. Experiments to obtain samples by covering the iron with mercury during the boring failed because the mercury contained occluded air. The ferrous oxide which is contained in the occluded slag is reduced when heated in a current of hydrogen; when the iron itself contains no ferrous oxide; this error, however, is of little importance, since slag is itself an objectionable constituent. The results cannot be controlled by weighing the sample before and after heating in a current of hydrogen, and ascertaining whether the loss in weight of the iron, multiplied by $\frac{8}{9}$, corresponds with the gain of the absorption apparatus, because the carbon and sulphur in the sample are also converted into volatile hydrogen compounds.

A. R. L.

Estimation of Sulphur in Iron. By W. SCHINDLER (*Zeit. angew. Chem.*, 1893, 11—13).—Meineke has attempted to prove that commercial iron, when treated with hydrochloric acid, does not yield all its sulphur as hydrogen sulphide, and that a not inconsiderable amount is left in the insoluble residue, and must be estimated. Hattensaur has, however, demonstrated that Meineke's ideas are incorrect, and that there is no reason to distrust the time-honoured hydrogen sulphide process of estimating the sulphur.

The author, having made a few experiments, states that Meineke has made the mistake of using an acid of insufficient strength (sp. gr. 1.1) and that this causes, indeed, an incomplete expulsion of the sulphur. By using a strong acid of 1.19 sp. gr., every trace of sulphur was obtained as hydrogen sulphide.

The author passes the gases evolved on dissolving the sample through a solution of bromine in hydrochloric acid, and afterwards estimates the sulphuric acid thus produced.

L. DE K.

Estimation of Nitrogen in Nitrates and in Nitric acid. By J. STOKLASA (*Zeit. angew. Chem.*, 1893, 161—163).—The author, having tried the recent processes for the estimation of nitrogen in nitrates, states that the methods proposed by Schlösing-Grandeau, Lunge, Stutzer, and Devarda all yield accurate results. If, however, the assay must be done in a very short time, it is best to use Lunge's nitrometer.

Another fairly rapid process is the one proposed by Devarda (compare this vol., ii, 343). Devarda's reducing alloy is readily prepared by melting in a Hessian crucible 50 parts of copper, and adding first 45 parts of aluminium and then 5 parts of zinc.

L. DE K.

Estimation of Phosphoric acid in Wines. By MORGENSTERN and A. PAVLINOFF (*J. Russ. Chem. Soc.*, 24, 341—346).—The authors estimate the phosphoric acid in wines directly (without evaporating and calcining) as follows:—200 c.c. of the wine is placed in a conical flask and boiled until most of the alcohol has been removed. To the hot liquid, 20 c.c. of nitric acid, sp. gr. 1.38, is added in portions, the boiling being continued until the oxides of nitrogen have been largely got rid of. On cooling, the liquid is neutralised with ammonia, 50 c.c. of ammonium citrate solution, prepared according to Märker's direction, is added, and then 25 c.c. of magnesia mixture is dropped in with continual shaking. Ammonium magnesium phosphate separates almost at once as a finely crystalline, easily washed precipitate, which gives a perfectly colourless pyrophosphate on ignition.

The results obtained in this way agree with the determinations made by the molybdate method in the ash within about 1 milligram of P_2O_5 in 100 c.c. of wine.

J. W.

Analysis of Bone Meal, Fish Guano, and similar Phosphatic and Nitrogenous Manures. By W. HESS (*Zeit. angew. Chem.*, 1893, 74—79; 148).—The author points out how difficult it is to get a thoroughly trustworthy sample. In order to get the exact relation between the phosphoric acid and the nitrogen, the estimation of these

constituents should be effected in such a way that only one weighing-out is required. 5 grams of a well mixed sample is heated in a Kjeldahl flask with 35 c.c. of strong sulphuric acid and 0.5—1 gram of mercuric oxide, and then boiled for about $1\frac{1}{2}$ —2 hours until decomposition is complete. After diluting with water, the contents are made up to 500 c.c. For the estimation of the nitrogen, 200 c.c. (= 2 gram substance) is distilled with aqueous soda and the ammonia estimated as usual.

For the estimation of the phosphoric acid, 50 c.c. of the filtered solution is mixed with 50 c.c. of Märker's solution of ammonium citrate and 20 c.c. of magnesium mixture. After a few hours, the precipitate is filtered off and treated as usual. L. DE K.

Preparation of Perchloric acid and Estimation of Potassium in presence of Non-volatile Acids by means of the same. By R. CASPARI (*Zeit. angew. Chem.*, 1893, 68—74).—The ordinary methods for the preparation of perchloric acid being somewhat costly and even dangerous, the author proposes the following process:—A Hessian crucible, 15 cm. in height, is filled with pure potassium chlorate, and is heated in a brick oven until the mass, liquid at first, has become a thickish paste. The fusion generally takes about $1\frac{1}{2}$ hours. The fused mass is reduced to powder and boiled with $1\frac{1}{2}$ times its weight of water. By this means the potassium chloride is dissolved, and, after cooling, the insoluble mass is rinsed with cold water and dried.

The potassium perchlorate is now dissolved in 7 times its weight of hot water and precipitated with a slight excess of hydrofluosilicic acid. After gently boiling for an hour, with occasional addition of hot water, the solution is allowed to cool and poured off from the jelly-like potassium silicofluoride. The liquid is evaporated on the water-bath and then allowed to remain in a cold place for 24 hours, which causes the separation of any remaining potassium compound. Solution of barium chloride is now added until precipitation ceases, and the filtrate is again evaporated until whitish fumes make their appearance. It is then filtered from any traces of potassium or sodium perchlorate, the filtrate is freed from barium by the cautious addition of sulphuric acid, and after standing for a few days, the reagent is ready for use.

Estimation of Potassium in presence of Non-volatile Acids.—The author fully confirms the statement of Wense (this vol., ii, 46), that potassium perchlorate is practically insoluble in commercial absolute alcohol to which 0.2 per cent. of perchloric acid has been added. He also has proved the complete solubility of the perchlorates of iron, aluminium, and calcium, and even of lead, although the alcoholic solution of the latter soon decomposes. The author objects to the use of weighed paper filters, but uses a weighed asbestos filter.

The process seems applicable, not only in presence of volatile acids, such as nitric or hydrochloric, but also of non-volatile acids, such as phosphoric, boric, oxalic, or tartaric, provided they are soluble in alcohol. Sulphuric acid does, however, interfere, but may be removed by the cautious addition of barium chloride.

When estimating potassium in presence of phosphoric acid by

evaporating with perchloric acid, and extracting the residue with the acid alcohol, a little phosphoric acid is liable to remain insoluble, but it may be completely removed by a second treatment with the perchloric acid.

L. DE K.

Analysis of Crude Salt and Brines and Calculation from the Analytical Data. By J. WIERNIK and S. WIERNIK (*Zeit. angew. Chem.*, 1893, 43—47; 148).—The real object of an analysis of crude salt, or its mother liquors, is to find out the exact amount of sodium chloride it contains, but in the present state of affairs it is rather too much left to the discretion of the analyst how the results are to be calculated. In fact the operator may, if he chooses, calculate a certain amount of chlorine which really exists as sodium chloride into the comparatively worthless magnesium salt. The author proposes to estimate the amount of magnesium chloride directly, and this may be done very accurately by extracting the sample with absolute alcohol, which readily dissolves the magnesium chloride, but leaves the sodium compound undissolved. The magnesium salt may be calculated either from the weight of the magnesium pyrophosphate obtained from it, or more conveniently from the amount of chlorine.

When dealing with brines, these should be first evaporated to dryness.

L. DE K.

Quantitative Analysis by Electrolysis. By A. CLASSEN (*Zeit. anorg. Chem.*, 3, 211—219).—The author criticises some of the methods proposed by Rüdorff (this vol., ii, 93), and objects to the statement that electrolytic methods heretofore published contradict each other, and are of little value.

A. G. B.

Electrolytic Analysis. By F. RÜDORFF (*Zeit. anorg. Chem.*, 3, 370).—A reply to Classen.

Estimation of Aluminium in Ferroaluminium. By H. v. JÜPTNER (*Chem. Centr.*, 1893, i, 665; from *Öst. Zeit. Berg.- u. Huttenwesen*, 41, 110—112).—The estimation of aluminium in samples of ferroaluminium containing a large percentage of this metal may be conducted as follows:—The sample is dissolved in sulphuric or hydrochloric acid, and the silica separated as usual; a portion of the solution is oxidised and ammonia added, and the precipitate containing aluminium and ferric oxides and phosphoric acid is weighed, the iron being estimated by titration in another portion, whilst in a third the phosphoric acid is estimated. The percentage of aluminium is thus arrived at by a simple calculation. A sample analysed by this method gave Al = 12.31 per cent. and by Neuhausen's method it gave Al = 12.64 per cent.

A. G. Neuhausen's Method.—5 grams of the sample is dissolved in dilute sulphuric acid, the solution evaporated to dryness, the residue taken up with a little sulphuric acid, and diluted to 300 c.c. of the filtrate is reduced with iron wire, neutralised with sodium carbonate, and poured into mixed boiling solutions of potassium cyanide and potassium hydroxide: for 1 gram of substance, 20 per cent. potash (50 c.c.) and 20 per cent. potassium cyanide (40 c.c.) are

used. The precipitate is collected and washed well, or the liquid is diluted to 500 c.c., filtered, and to 300 c.c. of the filtrate (= 1 gram substance) ammonium nitrate together with $1\frac{1}{2}$ times its amount of potash added, heated for an hour, and the alumina collected and washed. It must be tested for potash and iron; the latter must be estimated by dissolving the precipitate in concentrated hydrochloric acid and titrating with stannous chloride and iodine solutions, or with potassium thiosulphate after digestion with potassium iodide. All the reagents must of course be tested for aluminium.

A. R. L.

Chemical Investigation of Steel. By L. SCHNEIDER (*Chem. Centr.*, 1893, i, 365—366; from *Öst. Zeit. Berg.- u. Hüttenwesen*, 41, 15—17).—*Estimation of Phosphorus in Steel.*—2 grams of steel shavings are dissolved in nitric acid (sp. gr. 1.2; 30 c.c.) and a concentrated solution of potassium permanganate (2 c.c.) dropped into the boiling solution, the boiling being continued for a short time. The precipitated manganic oxide is dissolved by the addition of a few drops of ferrous sulphate solution, and the solution filtered from silica. To about 30 c.c. of the solution, double the volume of ammonium molybdate solution is added, and the mixture warmed on the water-bath at 80°. The flask is then fitted with a caoutchouc stopper, and the mixture shaken; after 10 minutes, the phosphomolybdate precipitate is collected, washed with ammonium nitrate solution, rinsed off the filter into a porcelain capsule with ammonia, evaporated, cautiously heated to expel the ammonium salts, and weighed: 0.012 gram of the precipitate is equivalent to 0.01 per cent. of phosphorus in the sample. The ammonium molybdate solution is prepared by dissolving molybdic anhydride (100 grams) in aqueous ammonia (300 c.c.), diluting with water (100 c.c.), pouring the solution into nitric acid (sp. gr. 1.2; 1250 c.c.), and stirring at a temperature of 85°.

. *Estimation of Phosphorus in Iron Ores, Slags, &c.*—2 grams of the pulverised sample is moistened with concentrated hydrochloric acid (10 c.c.) and evaporated in a platinum capsule with the addition of concentrated sulphuric acid (2 c.c.) and hydrofluoric acid (10 c.c.) until white fumes of sulphuric anhydride appear. The residue is boiled with nitric acid (sp. gr. 1.2; 10 c.c.) and water (20 c.c.). The filtrate is mixed with the molybdate solution, and the remainder of the operation conducted as already described.

The percentage of phosphorus may be estimated volumetrically as follows:—The phosphomolybdate precipitate is washed with water containing ammonium sulphate, and dissolved in ammonia; the solution is then acidified with hydrochloric or sulphuric acid, reduced with zinc, and titrated with potassium permanganate at a temperature of 40—50°. According to F. A. Emmerton, the quantity of permanganate corresponding with 100 parts of iron is equivalent to 90.7 parts of molybdic anhydride, or to 1.62 parts of phosphorus; whilst according to v. d. Pfordten, the same quantity of permanganate is equivalent to 85.7 parts of molybdic anhydride and 1.53 parts of phosphorus. The results calculated on Emmerton's values agree with those obtained by gravimetric analysis.

A. R. L.

Gas-volumetric Estimation of Nickel. By SYSSOYEFF (*Chem. Centr.*, 1893, i, 230—232; from *Mon. Sci.* [4], 6, 865—868).—A quantity of nickel salt corresponding with 0.25 gram Ni is dissolved in about 100 c.c. of water and treated with an excess of potassium cyanide, whereby a solution of potassium nickel cyanide, $K_2Ni(CN)_4$, is obtained. To this is added 1:2 sodium hydroxide solution (30—40 c.c. ?) and chlorine passed into the mixture, when the following reaction occurs, $2K_2Ni(CN)_4 + 3KClO + 6Cl_2 = 7KCl + 8(CN)Cl + Ni_2O_3$, and the nickelic oxide, which is all precipitated in a few minutes, is collected on an asbestos filter, and washed with warm, faintly alkaline water. The method consists in measuring the oxygen which results from the action of the oxide on hydrogen peroxide thus:— $Ni_2O_3 + H_2O_2 = 2NiO + H_2O + O_2$. It is carried out in a modified Lunge's gas-volumeter, which is described with the aid of a drawing. The separation of nickel and iron is effected by Moore's method (*Abstr.*, 1888, 631). A. R. L.

Nickel Analysis. By S. H. EMMENS (*J. Anal. Chem.*, 6, 643—650).—By the electrolytic precipitation of copper from acid solutions containing nickel, the latter metal is also thrown down when a strong current is employed. The author recommends the precipitation of the copper as sulphide, and, from the filtrate, after oxidation that of the iron, &c., as hydroxide; if much iron is present, the washed precipitate is boiled with a very small quantity of dilute sulphuric or hydrochloric acid, whereby the whole of the nickel together with a small quantity of iron is dissolved; the latter is then precipitated in the filtrate by ammonia and ammonium chloride. The iron precipitate may be boiled with dilute ferric sulphate solution instead of with dilute acid. A. R. L.

Potassium Ferrocyanide. Detection of Hydrocyanic acid in presence of Ferrocyanides. By W. AUTENREITH (*Arch. Pharm.*, 231, 99—109).—Potassium ferrocyanide is by no means so stable in the presence of dilute acids as is generally supposed; carbonic anhydride at 72—74° liberates hydrocyanic acid from it, potassium ferrous ferrocyanide, $K_2Fe_2(CN)_6$, being precipitated; artificial digestive fluid, peptone, and casein each exercise, at blood heat (37—40°), a similar action. Potassium ferrocyanide is not a poison; hydrocyanic is doubtless liberated from it in the stomach, and continuously, but in quantity so small that it is absorbed by the system as fast as formed, and undergoes further chemical change, so that a lethal dose has no time to accumulate. The only certain way to detect hydrocyanic acid or simple cyanides in presence of potassium ferrocyanide is to distil with a considerable amount of sodium hydrogen carbonate, and examine the distillate for hydrocyanic acid. If the presence of mercuric cyanide is suspected, a few c.c. of sulphuretted hydrogen water must be added, in addition to the carbonate, which does not itself decompose mercuric cyanide. C. F. B.

Higher Alcohols and other Impurities in Ethyl Alcohol. By E. GOSSART (*Compt. rend.*, 116, 797—800).—The author has de-

terminated the limits of sensitiveness of the capillary method of analysis (Abstr., 1892, 236) for the various impurities commonly found in ordinary alcohol. An alcohol will only roll in drops on its own surface when its strength is not less than 20° , and an alcohol of 20° will roll only on alcohol of a little more than 19° and a little less than 21° ; alcohol of 25° admits of somewhat wider limits; whilst from 40° to 90° an alcohol will roll upon another which does not differ from it by more than 5° . These results are independent of the impurities present in the alcohol.

The analytical method is based upon the fact that when n c.c. of an alcohol of N° is diluted with N c.c. of water, an alcohol of n° is obtained. If, therefore, the alcohol to be examined is stronger than 20° , 20 c.c. of it is gradually diluted with water, the volume added when it just begins and when it just ceases to roll on alcohol of 20° being carefully observed. The mean of the two volumes, N , gives the strength of the alcohol. When the alcohol is of a strength lower than 20° , 20 c.c. is mixed with 20 c.c. of alcohol of 39.2° , and water is added until the rolling begins and ceases, the volume required, P , in c.c., gives the strength in degrees.

For the detection of impurities, it is advisable to dilute the alcohol to 25° . In the case of amyl alcohol, a difference in composition of 0.5 per cent. prevents the rolling. The best standard is alcohol of 25° , containing 0.6 per cent. of amyl alcohol. Butyl alcohol behaves in a strictly analogous manner, and requires a similar standard liquid. In the case of propyl alcohol, the standard should contain 0.7 per cent. For acetone, the standard should contain 0.3 per cent., and alcohol of 25° containing less than 2 per cent. of acetone rolls on pure alcohol of 25° . For aldehyde, the sensitiveness is not sufficient to be of practical value, but the method may be usefully applied in the case of the impurities in tailings.

C. H. B.

Estimation of Phenols in Crude Carbolic acid. By G. SCHACHERL (*Chem. Centr.*, 1893, i, 324—325; from *Zeit. allg. österr. Apoth. Vereins*, 1892, 35).—Carbolic acid which is only slightly soluble in aqueous alkali (100 grams), or the purer kind, (50 grams), is shaken in a separating funnel with 9 per cent. aqueous sodium hydroxide (100 c.c.). The alkaline liquid is then run off, the oil once more extracted with 100 c.c., and, finally, two or three times with 50 c.c. of alkali. The combined alkaline extracts are mixed with an equal volume of water, and distilled until oily drops no longer pass over, indicating the absence of hydrocarbons; the residue is then acidified with hydrochloric acid and again distilled, using a large condenser, when the phenols pass over as a heavy oil. The distillation is stopped when the distillate measures 200 c.c., the oil is separated from the aqueous portion, and the latter returned to the distillation flask; the distillation is now again continued, and after a while interrupted, the oil being mixed with the first portion, and the aqueous layer returned to the distillation flask. The distillation is now repeated in this manner until the distillate no longer contains oily drops; the final aqueous distillate measures only 60—70 c.c., and is placed, together with the phenols, in a measuring cylinder. It is

shaken with an excess of common salt, allowed to separate into layers, and the volume of the upper layer, consisting of phenols, read off. The resinous substances remain in the distillation flask.

Carbolic acid of a still better grade (amount not stated) is introduced directly into the distillation flask, together with sodium hydroxide solution (300 c.c.) and treated as above described.

The mixture of phenols which has remained in contact with the sodium chloride solution contains 9 per cent. (by vol.) of water; since, however, phenols are soluble in concentrated brine, 5—6 per cent. too much cresol is found by direct reading. Red carbolic acid contains 11 per cent. of water, the technical product being, as a rule, saturated with water. By crude carbolic acid, the author means a product containing at least 50 per cent. of cresols.

A. R. L.

Estimation of Uric acid. By F. G. HOPKINS (*Proc. Roy. Soc.*, 52, 93—99; also *Chem. News*, 66, 106).—The urine is saturated with solid ammonium chloride (about 30 grams to 100 c.c.); the urates are precipitated as ammonium urate, which is collected, treated with hydrochloric acid, and the uric acid which separates out may then be estimated by any accustomed method.

This method is not only simpler and more rapid than others in use, but is as accurate as the standard Salkowski-Ludwig method.

W. D. H.

Recognition of the Radicle Benzoyl in Organic Compounds.

By E. LÉGER (*Bull. Soc. Chim.* [3], 796—798).—Ferreira da Silva devised a method for the detection of cocaïne, in which some milligrams of the substance is evaporated on the water-bath with nitric acid (sp. gr. 1.4), and the residue added to concentrated alcoholic potash, when the odour of peppermint is developed. Subsequently Béhal found that the compound formed is ethylic benzoate. The author finds that the same odour is developed by similarly treating benzoynaphthol, populin, aconitine, and other compounds containing the benzoyl radicle, a fact which renders the method useless as a specific test.

A. R. L.

Detection of Cineole in Ethereal Oils. By E. HIRSCHSOHN (*Chem. Centr.*, 1893, i, 503; from *Pharm. Zeit. Russ.*, 32, 49—51).—While experimenting on the solubility of iodole (tetriodopyrroline) in ethereal oils, the author observed that cajeput, camphor, eucalyptus, and other oils dissolved iodole at first, but a crystalline compound subsequently separated out, which was readily soluble in ether and alcohol, but only sparingly so in chloroform. This reaction is due to the presence of cineole in the oils. As a test, it is carried out as follows:—3 to 15 drops of the oil is introduced into a test-tube, and shaken with 0.01—0.05 gram of iodole. If dissolution does not occur, more of the ethereal oil is added drop by drop, and when a clear solution is formed, it is allowed to remain for 24 hours. The supernatant liquid is then poured from the crystals, which are washed with light petroleum, and subsequently boiled with potash, when the odour of cineole will be developed. A list of ethereal oils which did not exhibit the reaction is subjoined.

A. R. L.

Estimation of Fat in Milk. By WEISS (*Chem. Centr.*, 1893, i, 589—590; from *Pharm. Zeit.*, 38, 87).—30 c.c. of milk is introduced into a flask of 300 c.c. capacity, and then mixed with 3 grams of officinal sodium hydroxide solution; light petroleum (60 grams) is added in three portions, and the mixture shaken after each addition until the liquid is quite homogeneous. If the last portion of petroleum does not mix readily, the liquid is placed aside for $\frac{1}{4}$ hour, after which mixing is easily brought about. The emulsion may be kept without separating for a day, but after adding 20 grams of alcohol and shaking the liquid frequently, separation is effected in six hours, and at the end of 24 hours three liquid layers have formed: the lowest is clear, and of a yellow colour, the middle one somewhat turbid, whilst the upper one, which is clear and colourless, contains the whole of the fat. An aliquot weight of the latter (petroleum solution) is then evaporated in a flat dish at 50° , and the residue dried at 100° .

Instead of weighing the fat solution, 25 c.c. of the milk is shaken with 3 c.c. of sodium hydroxide solution, and subsequently with 3 portions of light petroleum (25 c.c. each). 50 c.c. of the fat solution is then evaporated, and the fat weighed and calculated to 100 c.c. of milk.

A. R. L.

Modification of the Reichert-Meissl Method. By H. KREIS (*Chem. Centr.*, 1893, i, 234—235; from *Schweiz. Wochenschr. Pharm.*, 30, 481—483).—The principle of this method is the saponification of the glycerides of butter fat by means of concentrated sulphuric acid; hydrolysis is effected thus much quicker than by means of potash.

Five grams of the anhydrous fat is melted in an Erlenmeyer's flask closed with a loose fitting stopper, and, after being heated in a water-bath at a temperature of 30 — 32° for some minutes, concentrated sulphuric acid (10 c.c.) is added. The flask, placed horizontally, is rotated round its vertical axis until the contents are quite clear, when it is replaced in the water-bath. At the expiration of 10 minutes, water (150 c.c.) is added, and the mixture distilled as in the Reichert-Meissl method.

A. R. L.

Goats' Milk and its Detection in Admixture with Cows' Milk. By SCHAFFER (*Chem. Centr.*, 1893, i, 620—621; from *Schweiz. Woch. Pharm.*, 31, 58—60).—The author finds from numerous analyses that the composition of goats' milk lies between the following limits:—Water, 86.74—90.46 per cent.; fat, 2.14—4.72 per cent.; milk-sugar, 2.07—4.77 per cent.; proteids, 2.3—4.38 per cent.; ash, 0.51—0.93 per cent. A sample of butter from goats' milk contained:—Water, 11.23 per cent.; fat, 87.38 per cent.; solids other than fat, 1.39 per cent.; the pure fat had a sp. gr. at 100° = 0.8668, and melted at 30° ; its saponification value (Köttstorfer) was 226; its Reichert-Meissl value, 24; and its refraction (Amagat and Jean), 31.5°. These values are too close to those obtained with cows' milk to enable the two to be differentiated. The most pronounced difference between the fats, besides their distinctive odour and taste, is the want of colour of the ethereal extract of the fat from goats' milk.

A. R. L.

Detection of Foreign Fats in Wool Fat. By W. GRAFF (*Chem. Centr.*, 1893, i, 504).—The author criticises Helbing and Passmore's method (this vol., ii, 351) adversely, and he states that it was employed in 1888 by Kremel. The saponification test can be conducted in a reflux apparatus, but the method can only be regarded as a qualitative test for glycerol. A. R. L.

Analysis of Bees-wax. By R. BENEDIKT (*Chem. Zeit.*, 16, 1922).—The author defends his modification of Hübl's process against the criticism of Röttger (this vol., ii, 351), but admits that for the detection of less than 5 per cent. of paraffin or ceresin, the process recommended by Buisine should be used (compare *Abstr.*, 1892, 1034). L. DE K.

Some Toxicological Reactions. By J. STERN (*Zeit. angew. Chem.*, 1893, 136—138).—1. Reactions of Oils of Pimento and Cloves.—The author has found that the two oils give the same reactions with ethereal solution of bromine, alcoholic hydrochloric acid, sulphuric acid, Fröhde's reagent, ferric chloride mixed with sulphuric acid, nitric acid, picric acid, lime water, and alcoholic solution of ferric chloride. When in a fairly pure state, the oils may be distinguished by their odour, but when isolated from the contents of a stomach, the smell is generally too much obscured to be trustworthy.

2. Behaviour of Strychnine Nitrate with Hydrochloric acid.—The author points out that the reddish colour generated by heating strychnine nitrate with hydrochloric acid is also given by sugar, which renders the test practically worthless in toxicological investigations. L. DE K.

The Estimation of Emetine in Ipecacuanha Root and in the Fluid Extract of the same. By C. C. KELLER (*Chem. Centr.*, 1893, i, 235—236, 322—324; from *Schweiz. Wochenschr. Pharm.*, 30, 501—505 and 509—514).—The author has investigated several of the methods which have been proposed for the estimation of alkaloids in narcotic extracts, and he finally decides that Schweissinger and Sarnow's method (*Pharm. Centralh.*, 1890, 31, 771) is by far the best.

For the estimation of emetine in fluid extract of ipecacuanha, the mode of procedure is as follows:—8 grams of the extract is diluted with an equal weight of water, chloroform (32 grams), and ether (48 grams) added, and the mixture well shaken; ammonia (4 grams) is now added and the shaking continued for 30 minutes. After the mixture has settled, 50 grams of the chloroform-ether layer is filtered into a tared flask, distilled, and the varnish-like residue washed twice with 5—10 c.c. of ether; the emetine is then dried in a water-bath and weighed. After this, it is dissolved in hot absolute alcohol (10 c.c.), water added until a permanent turbidity is produced, and the liquid titrated with N/10 hydrochloric acid in the presence of hematoxylin solution until the colour is pure yellow. The results are calculated on the formula $C_{30}H_{40}N_2O_5$ (Kunz, *Abstr.*, 1887, 980), the equivalent value of which (254) was established by special experiments with pure emetine.

For the estimation of emetine in ipecacuanha root, the following method has been found to yield satisfactory results:—10 grams of the powdered root dried at 90–100° is shaken for some minutes in a dry glass vessel with a mixture of chloroform (40 grams) and ether (60 grams); on the addition of 10 grams of ammonia (official strength) and rotating the mixture, the suspended matter sinks to the bottom of the vessel, and the emetine is dissolved. The mixture is shaken for an hour, and, after this, another 5 grams of ammonia is added. 50 grams of the clear chloroform-ether solution is now distilled, the residue treated twice with 10 c.c. of ether, dried, and the emetine weighed. As, however, the root contains about 0·3 per cent. of fat, the presence of which vitiates the titration, this latter substance should be previously removed. To accomplish this, 10 grams of the dry, powdered root is placed in a small funnel which is plugged with a wad, and washed with 10–15 c.c. of ether until the filtrate is colourless. The residue is then washed into a tared glass with ether, and the latter, after being made up to 60 grams, is mixed with chloroform (40 grams), and the process conducted as above. The test analyses were satisfactory, and they show that the requirement of the Swiss Pharmacopœia, that ipecacuanha root should contain at least 2·5 per cent. of emetine, is not excessive. Choline, which Kunz and Arndt have found in ipecacuanha root, is neither extracted by ether (Dieterich) nor by a mixture of ether and chloroform.

The author promises to make known a simple method whereby an approximately quantitative yield of emetine may be obtained.

A. R. L.

A Sensitive Reaction for the Detection of Bile Pigments in Urine. By H. ROSIN (*Chem. Centr.*, 1893, i, 368–369; from *Berlin. klin. Wochenschr.*, 30, 106–107).—The Tiedemann-Gmelin test usually fails in those cases in which the presence of bile pigment is doubtful, and this is also the case when Fleischl's or Masset's modifications are employed. The author makes use of iodine for the detection of bilirubin in urine, the colouring matter being thereby oxidised to biliverdin, an observation due to Maréchal.

The process is carried out as follows:—An alcoholic solution of iodine is prepared by diluting 10 parts of tincture of iodine with 100 parts of alcohol. This reagent is then added to the urine, to be tested in such a manner that the two liquids do not mix; at the expiration of a minute, or even before, a grass-green ring will be formed at the surface of contact of the two liquids; it is permanent for an hour. In the absence of bile pigment, the urine is decolorised by the reagent, so that there is formed at the place of contact of the two liquids a bright yellow, or colourless, ring.

A. R. L.

Precipitation of Proteids from Blood preparatory to the Estimation of Sugar. By J. SEEGEN (*Chem. Centr.*, 1893, i, 369–370; from *Centr. Physiol.*, 6, 604–607).—After numerous experiments, the author finally adopted the following method:—To 50 c.c. of the blood, 5 c.c. of acetic acid (sp. gr. 1·04) is added, together with 8–10 times the volume of water; the mixture is heated to incipient boiling, 9–10 c.c. of a 20 per cent. solution of sodium

carbonate gradually run in, and the liquid kept in ebullition for some minutes, after which it is filtered through a conical linen bag. The coagulum is repeatedly washed with water, the linen filter pressed, and the filtrate and washings concentrated to a known volume and finally filtered. It is now quite clear, and remains so on testing with acetic acid and potassium ferrocyanide; when acidified with hydrochloric acid and treated with potassiomeric iodide, however, a more or less copious precipitate is produced. The solution is well adapted for titrating.

A. R. L.

A Sensitive Reaction for the Detection of Albumin in Urine.

By E. SPIEGLER (*Chem. Centr.*, 1893, i, 368; from *Centr. klin. Med.*, 14, 49—52; compare *Abstr.*, 1892, 928).—The reaction is obtained by a solution of tartaric acid and mercuric chloride containing glycerol; 1 part of albumin in 250,000 may be detected by the formation of a white ring at the point of contact of the urine and the reagent. The author no longer employs sugar in preparing the reagent, as the latter is found to keep better without it. Urine containing iodine cannot be tested by the reaction; bromine compounds do not, however, interfere with it.

Under the influence of slight indisposition, the urine of certain persons otherwise in sound health contains frequently small amounts of albumin, which cannot be detected by the ferrocyanide-acetic acid test.

A. R. L.

Analysis of Rubber Goods. By R. HENRIQUES (*Chem. Zeit.*, 16, 1595—1596; 1623—1624; 1644—1645).—The author first points out the great difficulty of obtaining a fair sample. Soft rubber goods must be cut into tiny pieces, well mixed, and a fairly large quantity taken for analysis; hard rubber may be divided by means of a rasp. The estimation of the amount of ash is not always quantitatively useful. If the sample contains, say, siliceous matter, or barytes, the results are fairly accurate; but if the mineral matter consists of lead carbonate, red lead, &c., the ash found will be too low and cannot, of course, serve as a measure for the amount of true rubber. Then again, even supposing the ash to represent the true amount of mineral matter, there is no certainty that the rubber does not, to a certain extent, consist of other organic matter, or so called rubber substitute. Another difficulty is the presence of sulphur which may afterwards wholly, or partially, be found as an apparent constituent of the ash.

The author recommends the following process for the estimation of the total sulphur. A deep porcelain basin is covered with a funnel with a short stem, and 20 c.c. of fuming nitric acid is put into it. 3 or 4 grams of the finely cut up sample is then by degrees introduced through the opening of the funnel. When the violent action is over, the dish is warmed on the water-bath, the solution is evaporated to a syrup and then treated with 4 grams of a mixture of 3 parts of potassium nitrate and 4 parts of sodium carbonate. After drying is complete, the mass is gently fused until all carbonaceous matter has disappeared. The mass is now treated

with hydrochloric acid, evaporated to dryness to render silica insoluble, and then taken up with dilute nitric acid. If, as usual, an insoluble residue remains, it consists of silica, barium sulphate, and lead sulphate, the latter of which may be dissolved out by means of ammonium acetate, and added to the main solution. The silica and barium sulphate are separated by the usual method, and should the main fluid contain sulphates there cannot be any further quantity of barium. The sulphuric acid is now estimated in an aliquot part of the acid filtrate by means of barium chloride. Another portion of the filtrate is used for the estimation of any metal supposed to be present.

To ascertain how much sulphur is present as vulcanising sulphur, as distinct from metallic sulphides or sulphates, the author uses the following process:—Commercial light petroleum is shaken with aqueous soda to remove sulphur compounds, dried, and distilled, the fraction coming over between 140—250° being collected. 5 grams of the sample, or 12 grams if it is rather low in ash, is placed in a weighed 250 c.c. flask, and 150 c.c. of the petroleum is added. After connecting the flask with a reflux condenser, it is heated in an oil-bath up to 140—150°, until the rubber is quite disintegrated and an insoluble deposit has formed at the bottom of the flask. A higher temperature should be avoided to prevent formation of hydrogen sulphide. After cooling, the solution is poured through a weighed filter, and the residue is washed a few times, finally with light petroleum of low boiling point. The flask and filter are now both dried at 110° and reweighed, and the amount of insoluble matter is thus obtained in which the sulphur may be estimated as directed. The difference between the two estimations represents the vulcanising sulphur.

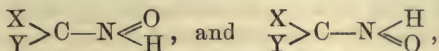
As regards rubber surrogates, the author has come to the conclusion that alcoholic soda is the most convenient reagent. 3—5 grams of the finely cut up sample is digested with 10 times its weight of 8 per cent. alcoholic soda in a reflux apparatus. The solution is diluted with water and evaporated in a dish until the alcohol is expelled. The insoluble residue is now collected on a weighed filter, dried at 100°, and weighed. As it always contains mineral matter, besides a little soda which washing has failed to remove, the ash should be taken (ammonium nitrate being employed), and a sulphur estimation should then be made. As hard rubber is but imperfectly soluble in light petroleum, its inorganic constituents cannot be separated by this process, but rubber surrogates may be extracted by alcoholic soda. It is as yet impossible to ascertain what proportion of the vulcanising sulphur belongs to the rubber and what to the surrogate.

L. DE K.

General and Physical Chemistry.

Determination of the Intensity of Rays. By N. TECLU (*J. pr. Chem.* [2], **47**, 568—583).—Crookes' radiometer has been adapted by the author for the purpose of determining radiant transparency (diaphanity). The radiometer is so arranged that its velocity of rotation is determinable, there being proportionality between the velocity of rotation and the intensity of the light falling on the radiometer. Tables are given showing the relative transparencies of different liquids. H. C.

Molecular Refraction of Compounds containing Nitrogen (Aldoximes and Ketoximes). By C. TRAPESONZJANZ (*Ber.*, **26**, 1428—1433).—The author has determined the molecular refractions of a number of aldoximes and ketoximes, with the view of obtaining evidence as to whether the nitrogen in these compounds is behaving as a triad element, or as suggested by Bischoff in the stereoisomeric formulæ



as a pentad. For sodium light and using the Lorenz formula, the molecular refraction of the group NOH was found to be in the aldoximes 6·575 and in the ketoximes 6·518, the mean value being 6·538. If for the atomic refraction of nitrogen the value, 2·870, given by Loewenherz be accepted and the atomic refractions $\text{O}' = 1·521$ and $\text{H} = 1·051$, the calculated value for the group NOH is 5·442. The difference between this and the observed value may either be due to the increment for the double linkage between carbon and nitrogen, for which Brühl has given the value 0·92—1·11, or if instead of O' we take $\text{O}'' = 2·287$, the calculated value then becomes 6·208, and no longer differs so considerably from that observed.

H. C.

Spectra of the Flames of some Metallic Compounds. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **52**, 117—123).—Nickel carbonyl, when mixed with hydrogen and burnt in oxygen at a porcelain jet, exhibits a spectrum which consists of two parts, (1) the spectrum of the main body of the green flame, and (2) that of the base of the flame. The spectrum of the main body consists of a series of shaded bands, brightest in the green, but extending on the red side beyond the red lithium line, and on the violet side well into the blue. These bands have their sharp edges on the more refrangible side. Besides the bands, a few visible lines appear, only one of which, λ 5476, is a known line of nickel. In the ultra-violet part, however, a great number of nickel lines were photographed. In the spectrum of the base of the flame there are two principal groups of lines, one in the orange and red, the other in the citron and yellow. None of them appear to be nickel lines.

Zinc ethide, when burned with hydrogen so as to reduce the luminous spectrum, showed the following zinc lines, λ 4812, 4721, and 4681. There were no lines of zinc in the ultra-violet.

J. W.

Flame Spectra of some Metals. By D. COCHIN (*Compt. rend.*, 116, 1055—1057).—The author has photographed the ultra-violet portion of the flame spectra of the salts of certain metals, using a spectrograph with quartz prisms and quartz and Iceland spar lenses, the sensitive gelatinobromide film being curved so that all the rays were in focus. In all cases the water-bands at λ 309 were obtained, but in no case were there any lines or bands of higher refrangibility even with somewhat longer exposures. With a hydrogen flame, the spectra are somewhat more luminous, but the results are practically the same.

Lithium gives the line at λ 413. Sodium gives the double line λ 330.3 and 330.2 obtained by Kayser and Runge in the electric arc. Potassium gives the lines λ 404 and 344.4. Rubidium, in addition to the visible line λ 420, gives the two doublets, observed by Kayser and Runge, at λ 359.1—358.7 and 335.1—334.8, especially if the hydrogen flame is used. Cæsium gives the lines λ 388, λ 361.5, and λ 347.75 in addition to the visible blue lines λ 459.7—450. The first two correspond with two pairs mentioned by Kayser and Runge, whilst the third also seems to correspond with a line seen by them.

Calcium, strontium, and barium give the visible lines in each case, but no ultra-violet lines.

Thallium, on the other hand, resembles the alkali metals in giving lines in the ultra-violet at λ 353 and 378.

C. H. B.

Leclanché Battery. By A. DITTE (*Compt. rend.*, 116, 984—986).—When the zinc platinum couple is immersed in a solution of ammonium chloride (compare this vol., ii, 355), not only is the solution decomposed and the zinc oxidised, but the zinc oxide can act on the alkali chloride. At the ordinary temperature, the decomposition is more rapid the stronger the ammonium chloride solution. Hydrogen is evolved and compounds are formed which contain zinc oxide and ammonia in proportions that depend on the concentration of the solution. Apart from secondary reactions, the decomposition of ammonium chloride by zinc is exothermic. No precipitate is formed, because the zinc oxide is soluble in ammonia solution, but ammonia tends to accumulate in the upper part of the liquid and zinc chloride in the lower layers. The resistance is lessened, and decomposition accelerated by substituting for the plate of platinum a porous cell containing a mixture of carbon and manganese peroxide. With a solution containing 10 per cent. of ammonium chloride, the secondary product is $2\text{NH}_4\text{Cl}, 4\text{ZnO}, 9\text{H}_2\text{O}$, which crystallises as soon as the solution is saturated. When only a small quantity of ammonium chloride remains, zinc oxide separates and mixes with the crystalline compound. If the original solution contains 15 per cent. of ammonium chloride, the crystalline product is $2\text{NH}_4\text{Cl}, \text{ZnO}$, which tends to separate at first in the upper part of the liquid. In the lower part of the liquid there is very little free ammonia, and a double zinc ammonium

chloride is formed, and by reason of its specific gravity tends to remain at the bottom of the vessel, and thus accelerate the solvent action on the lower part of the zinc.

C. H. B.

A Cadmium and Ammonium Chloride Battery. By A. DITTE (*Compt. rend.*, 116, 1128—1131).—The electrolysis of a solution of ammonium chloride by a cadmium platinum couple is exothermic, even when the heat of formation of the double ammonium cadmium chloride is left out of account. The ammonia tends to accumulate in the upper part of the liquid and the cadmium chloride in the lower part, but since cadmium oxide forms most rapidly where the ammonia is present, the upper part of the liquid becomes saturated with the compound $2\text{NH}_4\text{Cl}, \text{CdO}$, which crystallises at the surface.

The substitution of an agglomerate of manganese peroxide, or a porous cell containing the peroxide, for the platinum, accelerates the change, and a layer of crystals of the compound $2\text{NH}_4\text{Cl}, \text{CdO}$ forms round the upper part of the zinc rod. The cadmium chloride tends to accumulate in the lower part and the ammonia in the upper part of the liquid, but at some intermediate point the two products are present in the proportions required to form the compound $2\text{NH}_4\text{Cl}, \text{CdO}$, and the latter separates out gradually, forming a kind of diaphragm dividing the liquids into two parts of different composition. Since, however, in this layer the resistance is smaller than in any other part of the liquid, the cadmium is more rapidly attacked at this point than anywhere else.

The manganese peroxide seems to have no other function beyond that of rapid depolarisation.

C. H. B.

Voltaic Cells with Fused Electrolytes. By J. BROWN (*Proc. Roy. Soc.*, 52, 75—91).—In instituting a comparison of the observed electromotive forces of cells with their theoretical values, as given by "Thomson's law," the simpler the construction of the cell, the easier it is to ascertain the nature of the chemical action, on which the calculation rests. In cells with aqueous electrolytes, the solvent introduces several irreducible complications, arising from possible action of the solvent itself as an electrolyte, from the formation of insoluble films (either inactive and protective, as oxides, or active, as hydrogen) or from the uncertainty of calculations involving heats of solution of the products of voltaic reaction.

When the liquidity of the electrolyte is produced by fusion instead of by dissolution, these complications are to a large extent avoided; and, as a matter of experiment, two fluid cells made up of metals, immersed each in its fused chloride, give results nearer the "theoretical" values than those obtained with aqueous solutions. This is specially noticeable in the case of metals with high heats of oxidation, for example, magnesium and aluminium.

The electromotive forces of cells containing pairs of the metals tin, lead, and zinc come out nearest to the theoretical values. The other metals which were tried did not give so close an agreement, but could be brought into agreement by applying constant corrections, one for each metal; and reasons are given for attributing these corrections to

the high temperatures of the cells, as compared with the temperatures for which the recognised heats of combination are true.

Four of the cells were tested by passing currents through them in both directions alternately, and noting the electromotive force after the passage of each current. Polarisation was observed in the case of zinc-silver; in the others it was practically absent. J. W.

Changes at the Boundary between Solutions of Different Concentration during the Passage of an Electric Current. By G. H. ZAHN (*Ann. Phys. Chem.* [2], 48, 606—624).—The author has investigated the phenomenon of the separation of precipitates at the boundary of electrolytes (compare Kümmell, *Abstr.*, 1892, 1038). The current was allowed to pass through two solutions of the same salt of different concentrations, from that of the greater to that of the less, a separation of the hydroxide of the metal then taking place at the boundary of the two solutions in certain cases. Such a separation was noticed with salts of magnesium, calcium, barium, strontium, aluminium, manganese, iron, zinc, and copper, but not in the case of silver salts. In the latter case, however, as also with the salts of sodium and potassium, which form soluble hydroxides, the presence of the hydroxides at the boundary between the solutions could be rendered evident by the alkaline reaction of the solution with methyl orange at this point. The author is inclined to regard the above phenomena as evidence that water plays some part in the electrolysis of salt solutions. H. C.

Electrochemical Effects on Magnetising Iron. By T. ANDREWS (*Proc. Roy. Soc.*, 52, 114—117).—Two steel bars were cut adjacently from a long, finely-polished rod, so that they were as nearly as practicable alike in general composition and structure. Both were weighed and immersed in equal quantities of cupric chloride solution, one of them being previously magnetised. After a certain time (6 to 24 hours) they were removed from the solution, freed from deposited copper and carbonaceous matter, dried, and again weighed. In every case, the magnetised bar had lost more in weight than the unmagnetised bar, an average of 29 experiments showing an increase of corrosion in the steel due to magnetic influence of about 3 per cent. under the conditions of experiment. The bars were not highly magnetised. J. W.

Law of Dulong and Petit. By F. RICHARZ (*Ann. Phys. Chem.* [2], 48, 708—716).—The author gives a deduction of the law of Dulong and Petit based upon the Clausius virial theory. H. C.

Specific Heat of Boron. By H. MOISSAN and H. GAUTIER (*Compt. rend.*, 116, 924—928).—Pure amorphous boron was used, and it was mixed with small, lenticular masses of platinum with a view to increase the conductivity. The experiments were made with an ice calorimeter, and the following values were obtained:—At 100°, 0·3066; at 192·3°, 0·3407; and at 234·3°, 0·3573. The curve representing these results is almost a straight line, and the mean value

between 0° and 100° is 0.3066; between 100° and 192.3° , 0.3776; and between 192.3° and 234.3° , 0.4333. The corresponding atomic heats are 3.372, 4.153, and 4.766.

The mean specific heat between 0° and 100° is higher than that found by Weber, but the corresponding atomic heat is only 3.372. The specific heat, however, rises with the temperature, and extrapolation indicates that the atomic heat would be 6.4 at about 400° .

C. H. B.

Ferric Chloride and Ferric Oxalate Solutions: Distribution of Ferric Iron between Hydrochloric and Oxalic acids. By G. LEMOINE (*Compt. rend.*, 116, 880—882).—When a solution of ferric chloride containing 4 gram-atoms of iron per litre is diluted with water, there is considerable development of heat, which, however, cannot be due to hydration, because it is observed on dilution of a solution containing $\text{Fe}_2\text{Cl}_6 + 108\text{H}_2\text{O}$. The development of heat is due to the gradual decomposition of the ferric chloride with formation of hydrochloric acid and soluble ferric hydroxide. This view is confirmed by colorimetric observations, by means of which the amount of alteration can be estimated. The following table shows the percentage alterations at various degrees of dilution. N represents a degree of concentration corresponding with a solution containing 56 grams of iron per litre.

	4N.	3N.	1.5N.	N.	$\frac{1}{2}$ N.	$\frac{1}{4}$ N.	$\frac{1}{10}$ N.
Percentage amount of ferric chloride un- decomposed	100	74	50	46	37	35	29

The development of heat on dilution is much less marked with solutions of other ferric salts. At the ordinary temperature, dilution of ferric oxalate solution is accompanied by a slight absorption of heat, but if dilution takes place at about 80° , there is a slight development of heat.

The heat of formation of ferric oxalate from ferric oxide and oxalic acid is 34.8, but in concentrated solutions it is somewhat lower.

Oxalic acid to a large extent displaces hydrochloric acid when added to a solution of ferric chloride.

C. H. B.

Decomposition of Oxalic acid by Ferric Salts under the influence of Heat. By G. LEMOINE (*Compt. rend.*, 116, 981—983).—When ferric chloride and oxalic acid in equal molecular proportions are dissolved in water and heated, decomposition is insignificant at 40 — 50° , slow at 100° , but rapid in sealed tubes at 120° . At the ordinary temperature, only 0.019 of the mass was decomposed after six years. Water accelerates the decomposition, but the influence of dilution diminishes somewhat with the temperature. Excess of oxalic acid retards the change, but excess of ferric chloride accelerates it. Ferric sulphate and oxalic acid behave in a similar manner, but decomposition is somewhat slower, and the acceleration produced by water is much less marked.

Ferric oxalate in solution decomposes at 100° with separation of

ferrous oxalate. The velocity of the reaction at 100° is represented by the equation

$$\frac{dy}{dt} = a \left(1 - \frac{y}{p} \right)^n = 0.47 \left(1 - \frac{y}{p} \right)^{4.4},$$

and it is noteworthy that the initial velocity, 0.47, is greater than in the case of ferric chloride and oxalic acid. When hydrochloric acid is added, the velocity approaches that of mixtures of ferric chloride and oxalic acid; and with a large proportion of the acid the reaction is almost arrested. Excess of water accelerates the change somewhat, but oxalic acid retards it.

The phenomena observed depend to a large extent on the decomposition of ferric salts by water, and the reverse action produced by the free acid present.

C. H. B.

Some Applications of Raoult's Law at the Boiling Point of Solutions. By A. P. PAŘÍZEK and O. ŠULE (*Ber.*, 26, 1408—1412).—The molecular weights of several of the fatty acids and their ethereal salts were determined from the boiling points of their solutions in benzene. In the case of the acids, the molecular weight obtained increases with the concentration of the solution, and eventually approximates to double the ordinarily accepted value. The ethereal salts give normal values in dilute solutions, the agreement being closer the higher the boiling point of the salt in question.

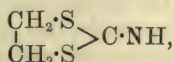
Water added to boiling alcohol causes first of all a depression and not a rise in the boiling point. The change Δt in the boiling point can be very well represented as a quadratic function of the percentage P of water in the alcohol $\Delta t = -0.0411P + 0.004348P^2$.

Rhamnose dissolved in alcohol gave a mean molecular weight of 206. This value points to the formation of an ethoxide, since $C_6H_{13}O_6Et = 210$, but $C_6H_{14}O_6 = 182$. The molecular weight of rhamnose was also determined from its effect on the boiling points of methyl and isopropyl alcohols. It was necessary, in the first place, to determine the molecular rise in the boiling points of these two liquids, for which experiments were made with benzaldehyde, aniline, and dimethylaniline. The values found were for methyl alcohol 9.20° , and for isopropyl alcohol 12.9° . Rhamnose gave in methyl alcohol solution a molecular weight 206, but in solution in isopropyl alcohol only 182. It appears, therefore, to form a methoxide, but no compound with isopropyl alcohol.

Water added to methyl alcohol causes only a rise in the boiling point. The molecular weight calculated from this is, however, abnormal, and lies between 31 and 37. Ethyl and isopropyl alcohols also give abnormal molecular weights in methyl alcohol solution. The value found for ethyl alcohol was between 110 and 118, and for isopropyl alcohol between 93 and 99. The formation of such molecular compounds as $EtOH, 2MeOH = 110$ and $Pr^iOH, MeOH = 92$ is probable.

H. C.

Coefficients of Affinity of Organic Bases. By E. LELLMANN and A. GÖRTZ (*Annalen*, **274**, 121—141).—A continuation of previously published work (Abstr., 1889, 1104; 1891, 638 and 1149). The values obtained with aniline both in more concentrated and more dilute solutions than previously used agree well, and the mean value is $\kappa = 67.5$. The observation that freshly prepared solutions give a value either too high or too low is confirmed; it may be due to the equilibrium between the four substances in solution not being immediately established, and to alterations brought about by external agencies (such as the formation of molecular aggregates) not yet known. The following mean values were obtained with other bases: Metaxylylidine, $\kappa = 106.7$; paraxylylidine, $\kappa = 72.79$; ortho-xylidine, $\kappa = 96.64$; ψ -cumidine, $\kappa = 117.6$; orthutoluidine, $\kappa = 51.63$; hexahydroquinoline, $\kappa = 59.76$; decahydroquinoline, $\kappa = 618.7$; ac.-tetrahydro- β -naphthylamine, $\kappa = 110.5$; metachloraniline, $\kappa = 20.85$; chlorotoluidine [$\text{NH}_2 : \text{Cl} : \text{Me} = 1 : 2 : 4$], $\kappa = 18.53$; chlorotoluidine [$\text{NH}_2 : \text{Cl} : \text{Me} = 1 : 4 : 2$], $\kappa = 32.26$; chlorotoluidine [$\text{NH}_2 : \text{Cl} : \text{Me} = 1 : 3 : 4$], $\kappa = 38.54$; orthobromaniline, $\kappa = 12.91$; metabromaniline, $\kappa = 24.87$; parabromaniline, $\kappa = 31.34$; bromotoluidine [$\text{NH}_2 : \text{Me} : \text{Br} = 1 : 2 : 4$], $\kappa = 28.48$; bromotoluidine [$\text{NH}_2 : \text{Me} : \text{Br} = 1 : 4 : 2$], $\kappa = 16.72$; glycocine, $\kappa = 17.56$; metamidobenzoic acid, $\kappa = 21.04$; picolinic acid, $\kappa = 9.75$; cytosine is a strong base, but gave results which varied widely; thiohydantoin, $\kappa = 10.58$; dimethylthiazole, $\kappa = 26.17$; the compound



$\kappa = 263.7$. Arranging the bases according to their increasing affinity coefficients, a series is obtained which deviates from that of Walker, whose determinations were made by the electrolytic method.

A. R. L.

Coefficients of Affinity of Organic Acids. By E. LELLMANN and J. SCHLIEMANN (*Annalen*, **274**, 141—156, 156—173).—Using the method previously described (Abstr., 1892, 1269), the authors have made measurements of the affinity coefficients of certain organic acids. Their results deviate from those of Ostwald obtained by the electrolytic method, but in support of them, it is urged that they indicate an unbroken diminution in the affinity from formic acid to caprylic acid. The following are the mean values: Normal butyric acid, $\kappa = 10.47$; caproic acid, $\kappa = 8.72$; caprylic acid, $\kappa = 7.63$. According to Ostwald, isobutyric acid is a stronger acid than propionic; the authors have, however, obtained the value $\kappa = 8.21$ as its affinity coefficient. Mandelic acid, $\kappa = 56.67$; dipyridylcarboxylic acid, $\kappa = 44.11$; phenylpyridinecarboxylic acid, $\kappa = 28.96$; sorbic acid, $\kappa = 13.02$; α -naphthoic acid, $\kappa = 21.62$. When a solution of phenylacetic acid is neutralised with barium hydroxide and examined in the usual way, the values obtained for the affinity coefficient vary according to the length of time the solution has been made; crystalline barium phenylacetate gave immediately after dissolution a mean value $\kappa = 19.68$, which remained constant after 18 days; the value

obtained for hydrocinnamic acid at the end of the same time was $\kappa = 13.85$.

The authors have also made some determinations of the affinity coefficients of acids by a spectrophotometric method in aqueous solution, using potassium metahydroxyanthraquinonesulphonate as indicator. The results are at variance with Guldberg and Waage's law; water does not, therefore, appear to be a suitable solvent for these determinations. Contrary to the dissociation degrees, the differences between the values for the affinity coefficients become greater with increasing dilution. Another series of experiments, in which dimethylamidoazobenzenesulphonic acid in aqueous solution was employed as indicator, leads the authors to the view that the chemical action is not proportional to the dissociation degree. Ostwald, by comparing the rate of hydrolytic action of acids with their electrical conductivities, arrived at an opposite conclusion. Certain acids are arranged in the order of their increasing strengths according to the authors' and to Ostwald's results; the two tables exhibit very large differences. The authors also reply to Arrhenius' criticisms (*Zeit. physikal. Chem.*, 10, 671) of their former work.

A. R. L.

Theory of Chemical Types. By F. FLAVITZKY (*Ber.*, 26, 1534—1538).—This paper adduces further evidence in favour of the author's theory of the correlation of the oxygen and hydrogen compounds of the elements (*Abstr.*, 1892, 1270). It is shown that the general type represents all the compounds of the elements, including the so-called molecular compounds, this being especially evident in the case of the halogen derivatives, such as the single and double haloid salts, with their water of crystallisation.

H. G. C.

Lectures on Inorganic Chemistry arranged in accordance with the Natural System of the Elements. By L. MEYER (*Ber.*, 26, 1230—1250).—In a lecture before the German Chemical Society, the author explains how, for some years past, he has made use of the periodic system in giving instruction in inorganic chemistry. He claims that the advantages obtained by making use of this method of classification are so great that he is now able to cover the whole of the ground in little more than 80 lectures, in spite of the fact that these are very fully illustrated by experiments.

The course commences with an explanation of the position occupied by chemistry among the other sciences, and of its relationship to these, and more especially to physics. A short historical account of the progress of chemistry follows, this being brought down to the time of Lavoisier, and serving to introduce an examination into the composition of air and of the nature of combustion. In connection with the phlogiston theory, hydrogen is brought forward, and the composition of water made the subject of investigation. The constancy in the combining proportions of hydrogen and oxygen by weight and by volume is exemplified, and the student in this way becomes acquainted with the eudiometer and with decomposition by electrolysis. The atomic theory is also briefly spoken of in this place. The elements oxygen, nitrogen, and hydrogen having been thus intro-

duced, the elements generally are spoken of, together with their distribution in Nature and relative importance. The laws in accordance with which they enter into combination with one another are considered at some length, the atomic theory being brought forward historically, and the laws of Dulong and Petit, and of Avogadro, are fully discussed. At the same time the historical treatment permits of the introduction of the electrochemical theory, in speaking of electrochemical equivalents and Faraday's laws of electrolysis.

The meaning of atomic weights being now rendered evident, the arrangement of the elements in the periodic system is at once explained. The author then starts with a consideration of the compounds of hydrogen with the elements, beginning first with those of Group VII, this serving to illustrate practically the similarity to be looked for in analogous compounds of elements belonging to the same group, and also the regular change in valency in passing from one group to the next. After these preliminaries, the elements and their compounds are considered *seriatim*, commencing with Group I in the periodic system. It is considered advisable, however, in dealing with the elements in this manner, to reserve the heavy metals in the first four groups to be discussed at a later period, the sub-groups being first alluded to when Group V is reached, and then subsequently taken in the following order :

V.	VI.	VII.	VIII.	I.	II.	III.	IV.
V,	Cr,	Mn,	Fe, Co, Ni,	Cu,	Zn,	Ga,	Ge,
Nb,	Mo,	—	Ru, Rh, Pd,	Ag,	Cd,	In,	Sn,
Ta,	W,	—	Os, Ir, Pt,	Au,	Hg,	Tl,	Pb.

Under the headings of the metals only those compounds are considered which may be regarded as derived from the hydrogen compounds previously spoken of, as, for instance, the oxides, sulphides, and chlorides. Salts of the oxy-acids are taken when the acid itself is under discussion, the author being inclined, from practical experience, to look on this as the better method of treatment, and one by means of which useless repetition may be avoided.

H. C.

Explosives. By H. BILTZ (*Ber.*, 26, 1378—1383).—There are certain explosives, such as nitroglycerol, dynamite, guncotton, picric acid, and the new German military powder, which, when simply heated, burn quietly if freely exposed, or, if confined, explode only at the spot where heat is applied without the whole mass taking part in the explosion. This is probably because they are bad conductors of their own explosive wave. If, however, the same substances are subjected to a violent shock by the explosion in their midst of initial charges of mercury fulminate, the shock seems to affect all the molecules of the explosive at once, and the whole mass of the latter explodes with enormous violence.

Descriptions are given of lecture experiments to illustrate these phenomena.

C. F. B.

Inorganic Chemistry.

Densities and Molecular Volumes of Chlorine and Hydrogen Chloride. By A. LEDUC (*Compt. rend.*, **116**, 968—970).—The hydrogen chloride was prepared by the action of concentrated sulphuric acid on fused sodium chloride, and dried over phosphoric anhydride; its density is 1.2696, and its molecular volume (oxygen = 1) is 0.9923.

The chlorine was obtained from a vessel of liquefied chlorine, a part of which had previously been allowed to evaporate. Hydrogen chloride was removed by means of cupric sulphate, and the chlorine was dried over concentrated sulphuric acid. Its density is 2.4865, and its molecular volume 0.9854.

The values in both cases differ considerably from those usually given.
C. H. B.

Combination of Oxygen and Hydrogen. By H. N. WARREN (*Chem. News*, **67**, 195).—1 c.c. of acidified water was introduced into small, selected glass tubes $1\frac{1}{2}$ inches long, into one end of which two platinum wires were fused, whilst the other end was sealed up. When these were subjected to the action of an electric current of 6 volts, the tubes rapidly burst owing to the heating of the liquid; when, however, one of the tubes was mounted within a strong glass vessel containing water, the action continued briskly for 25 minutes, when a vivid flash and violent explosion terminated the experiment. The author infers from many such experiments that under a pressure of 180 atmospheres free oxygen and hydrogen combine with great violence without the application of flame.
D. A. L.

Gravimetric Composition of Water. By W. DITTMAR and J. B. HENDERSON (*Chem. News*, **67**, 127, 139—141, 151—152, 164—167).—The authors have submitted the synthesis of water by the action of hydrogen on copper oxide to two series of rigorous quantitative experiments. Specially devised, accurately adjusted, and duly tested apparatus was employed, which could be securely sealed airtight by stop-cocks and india-rubber caps and stoppers. The mode of procedure was to charge the tube in which the reduction was to take place with about 115 grams of copper oxide, to heat it on a magnesia bath in a current of dry air, using about 4.5 litres, then to close it securely, and the next day exhaust it, admit hydrogen into it, allow it to assume the temperature of the balance case, exhaust again, measuring the vacuum, and weigh against a tare, prolonging the weighing so as to insure that no leakage of air was taking place, the exposed portions of india-rubber being protected by very thin silver foil during the weighing. The tube is then placed on a magnesia bath, and the water receptacle and various U-tubes adjusted; every trace of air is then eliminated by passing several litres of hydrogen through the cold apparatus, and the portions of the reduction tube which are not to be heated being properly protected, the heating is now proceeded

with, when the conversion into water ensues below redness; the water receptacle during the formation of water is immersed in an ice bath, which is replaced by a water bath at the temperature of the laboratory as soon as the copper oxide appears completely reduced, after which period the experiment is continued for a while to make certain that the reduction is quite complete; ultimately the apparatus is allowed to cool in a current of hydrogen before being detached. When detached, the hydrogen in the various pieces of apparatus is replaced by air dried by sulphuric acid; the tubes, &c., are then securely closed and weighed. The various weighings incidental to an experiment in the first series of syntheses were:—Reduction tube + copper oxide, reduction tube + copper, water flask before and after experiment, 1st U-tube, 2nd U-tube (sulphuric acid), and 3rd U-tube (phosphoric anhydride), both before and after; the last tube was found to be practically superfluous. From these weighings were deduced: the weight of oxygen consumed; the weight of water obtained, and the weight of hydrogen with which the oxygen had combined. These data were corrected for sulphurous anhydride carried in the hydrogen from the sulphuric acid used for drying the gas, and which amounted to less than 0.2 milligram per litre; for the air displaced by the water, copper, and copper oxide, taking the mean gravity of the former at 8.7016, and of the latter at 6.1418, whilst the composition of the latter, although not constant, was found to be in a sample $O + 1.0985Cu$, a number which was adopted for these calculations; and for the oxygen absorbed by the metallic copper when replacing the hydrogen in the reduction tube by dry air before weighing.* The methods of ascertaining the magnitude of these corrections are fully described in the paper.

After the authors had become aware of various sources of error, the second series of syntheses were started, in which hydrogen absolutely free from oxygen is employed, this being prepared by passing the gas (after its deoxidation by red-hot copper) over fused caustic potash, followed by phosphoric anhydride. These reagents placed in the same order after the water receptacle served to absorb the water vapour produced during the second series of experiments; therefore in this series there were only two U-tubes to weigh. Of course the purity of the water obtained was duly established. The authors discuss the results obtained very fully, and, excluding results in which there were irregularities in the experiments, they find that the amount of hydrogen required by 8 grams of oxygen equalled in 10 experiments 1.00879 grams, and in the seven best experiments 1.00848 grams, and they therefore adopt for the atomic weight of hydrogen $H = 1.0085$ ($O = 16$), or $O = 15.866$ or 15.87 ($H = 1$), as the net result of their work.

The paper concludes with a summary of the work of previous investigators on this point. The atomic weight of hydrogen ($O = 16$) was found to be 1.0075 by Stas, 1.0083 by Cooke and Richards, 1.0072 by W. A. Noyes, 1.0059 by Lord Rayleigh, and 1.0032 by E. H. Keiser.

D. A. L.

* In some instances a correction for occluded hydrogen is made.

Production of Hydrogen Peroxide during the Spontaneous Oxidation of Zinc: Combustion by Oxygen. By M. TRAUBE (*Ber.*, 26, 1471—1475).—The author has already shown (*Abstr.*, 1885, 1105) that small quantities of hydrogen peroxide are formed by the slow oxidation of zinc and other metals. This fact leads him to the view that during the slow oxidation of zinc, the water, and not the oxygen, is dissociated. The reaction may be represented as taking place in two stages (1) $\text{Zn} + 2\text{H}_2\text{O} + \text{O}_2 = \text{Zn}(\text{OH})_2 + \text{H}_2\text{O}_2$; (2) $\text{Zn} + \text{H}_2\text{O}_2 = \text{Zn}(\text{OH})_2$.

Schoenbein found that by shaking lead amalgam with very dilute sulphuric acid and air for 10 seconds, 95—98 per cent. of the theoretical amount of hydrogen peroxide was obtained, whilst at the end of 100 seconds only about half this amount was present. The following method was devised by the author in order to arrest the decomposition of the hydrogen peroxide as soon as it is formed. 500 c.c. of 3 per cent. milk of lime containing 1.33 per cent. of potash, 70 grams of mercury, and 10—20 milligrams of zinc in coarse powder previously amalgamated on the surface, are shaken together in a closed flask with air freed from carbonic anhydride. The zinc dissolves at first, then reprecipitates, and finally liquefies. As soon as this occurs, more zinc is added (16—20 milligrams at most) from time to time. In this way, all the hydrogen peroxide is precipitated as calcium peroxide, and its amount may, after acidifying a portion of the liquid, be ascertained by titration with permanganate. Similar results are obtained with barium or strontium hydroxides instead of calcium hydroxide, and with cadmium instead of zinc. This result is in accord with the author's electrolytic synthesis of hydrogen peroxide (*Sitzungsber. Akad. Berlin*, 1887, 1048). The hydrogen at the cathode immediately combines with the oxygen of the air, forming hydrogen peroxide, which is reduced to water by a further quantity of hydrogen. The difference is merely that in one case hydrogen is produced by the agency of zinc, and in the other by that of the electric current.

The observations of Dixon and of Baker that phosphorus, carbonic oxide, and carbon are only combustible in oxygen when water is present seem also to show that no dissociation of oxygen takes place, but that water when present undergoes decomposition. As a matter of fact, the author has shown (*Abstr.*, 1885, 1108) that the carbonic oxide flame contains hydrogen peroxide. The question whether the oxidation of hydrogen gas at a high temperature requires the presence of water must be left undecided for the present; at any rate, dissociation of oxygen occurs, for considerable quantities of hydrogen peroxide are present under certain circumstances in the hydrogen flame.

The author states, in conclusion, that hydrogen peroxide is only formed when oxidation is brought about by ordinary oxygen. Other oxidising agents (ozone excepted, see next abstract) do not give rise to the production of hydrogen peroxide. Palladium hydrogen, for example, in the presence of air and water yields hydrogen peroxide, whereas with permanganate solution water is formed directly. Compare Armstrong (*Proc.*, 1893, 145, *et seq.*). A. R. L.

Constitution of Hydrogen Peroxide and of Ozone. By M. TRAUBE (*Ber.*, 26, 1476—1481).—In the first portion of this paper the author upholds his view (*Abstr.*, 1886, 660) that hydrogen peroxide is a compound of 1 molecule of oxygen with 2 atoms of hydrogen. Hydrogen peroxide acts as an oxidising agent only towards powerfully reducing substances, such as zinc and sulphurous anhydride, with which it unites as $(OH)_2$. Schoenbein states that it does not react immediately with phosphorous acid or phosphorus, Weltzien found that a solution of hydrogen peroxide placed over phosphorus did not alter in titre after two months, and, according to Lustig, hydrogen peroxide has no action on alcohol, even in presence of dilute sulphuric acid. Hydrogen peroxide, in a very dilute solution, only slowly liberates iodine from potassium iodide, and the author finds that it does not oxidise normal potassium oxalate, even when boiled with it. If hydrogen peroxide consisted of two hydroxyl groups, it ought to be obtained by the electrolysis of barium hydroxide, but no trace of it appears at the anode, only active (atomic) oxygen.

Hydrogen peroxide and ozone are closely related, and the author assigns the formulæ " $2H.O=O$ " and " $O.O=O$ " to them respectively. In support of this formula for ozone, it is urged that in its reactions only 1 atom of oxygen is active, the others being evolved as ordinary oxygen.

Potassium tetroxide is a reducing agent towards acid solutions of permanganate, and decomposes directly into hydrogen peroxide when treated with acid without giving rise to active oxygen, for, if the decomposition takes place in the presence of indigosulphonic acid, the latter remains unaltered. The author therefore represents it thus, " $K.O=O.O=O.K$."

The author has already elsewhere proposed the name holoxides for compounds of the type of hydrogen peroxide. A. R. L.

Sulphuryl Peroxide (Holoxide). By M. TRAUBE (*Ber.*, 26, 1481).—By repeating his former experiments (*Abstr.*, 1891, 978), the author has obtained products which, on reduction, gave a ratio of active oxygen to sulphuric anhydride = 1 : 10, indicating ordinary persulphuric acid. It may be assumed from this that the compound SO_4 is only obtained when conditions are obeyed which have not at present been ascertained; its existence cannot for the present be insisted on. A. R. L.

Conditions of the Formation and Decomposition of Nitrous acid. By V. H. VELEY (*Proc. Roy. Soc.*, 52, 27—54).—The formation of nitric peroxide, which imparts the yellow tint to nitric acid, takes place in concentrated acids even at 30° , but with moderately dilute acids only at 100 — 150° , when the acid is not unduly exposed to sunlight.

The reaction between nitric oxide and nitric acid may be regarded as reversible, thus, $2NO + HNO_3 + H_2O \rightleftharpoons 3HNO_2$, when the solution is sufficiently dilute and the temperature low. For equilibrium, the ratio of the quantities of nitric and nitrous acids is about 9 : 1. With more concentrated acids, and at higher temperatures, the

chemical changes taking place are more complicated. In solutions containing both nitric and nitrous acids, the rate of change at any moment is proportional to the mass of the nitrous acid present, and is dependent on the ratio of the masses of nitrous and nitric acid, being the more rapid the greater the proportion of the former to that of the latter. In the particular case of the liquids prepared from nitric oxide and nitric acid, the rate of change was found to vary with the temperature according to the equation $v_t = vk^{t-t_1}$.

Nitrous-nitric acid solutions prepared in different ways behave in a similar manner as regards the diminution of the mass of the nitrous acid, but in other respects, such as the evolution of gases and action on metals, they are dissimilar. J. W.

Graphite. By W. LUZI (*Ber.*, 26, 1412—1414; compare Abstr., 1892, 406, 565, 945; and this vol., ii, 320).—Previous to the author's observation of the fact it was not known, as is implied in a statement of Moissan's (this vol., ii, 320), that there are certain varieties of graphite ("graphitite") which do not swell up when ignited with nitric acid.

Graphite from ordinary cast iron has been observed to swell up when ignited with nitric acid, although not in so marked a degree as in some other cases. C. F. B.

Rubidium Salts: a Correction. By W. MUTHMANN (*Ber.*, 26, 1425—1426).—For " RbSbCl_4 and CsSbCl_4 " (this vol., ii, 321) read " $3\text{RbCl}, 2\text{SbCl}_3$ and $3\text{CsCl}, 2\text{SbCl}_3$." C. F. B.

Fluorides of the Alkaline Earths. By C. POULENC (*Compt. rend.*, 116, 987—989).—Strontium chloride is decomposed by hydrogen fluoride at the ordinary temperature, with formation of an amorphous fluoride which only becomes indistinctly crystalline when heated in hydrogen fluoride at 1200° . Even at this temperature it does not volatilise.

Amorphous strontium fluoride is insoluble in cold water and almost insoluble in hot water; it is completely dissolved by boiling hydrochloric acid, but is much less easily attacked by nitric acid. Sulphuric acid converts it into strontium sulphate, and when heated in the air at 1000° , it is partially converted into the oxide. Hydrogen chloride decomposes it at a red heat, but water vapour or hydrogen sulphide is without action at this temperature. Alkali carbonates decompose it in the ordinary way. Its sp. gr. is 2.44.

When the amorphous fluoride is fused with alkali chlorides, it crystallises in octahedra, but is partially decomposed. When fused with potassium hydrogen fluoride, there is no decomposition, but the crystals are not so well defined. A mixture of equal parts of potassium hydrofluoride and potassium chloride, however, gives beautiful, transparent, regular octahedra. Strontium chloride, when fused with potassium hydrofluoride, yields simply crystallised strontium fluoride.

Barium fluoride is obtained in beautiful octahedra by fusing the

amorphous fluoride with potassium hydrofluoride and potassium chloride. Potassium chloride alone partially decomposes the barium fluoride with the formation of double salts. C. H. B.

Lead Tetrachloride. By H. FRIEDRICH (*Ber.*, **26**, 1434—1436; compare *Abstr.*, 1890, 699; also Classen and Zahorski, *Zeit. anorg. Chem.*, **4**, 100).—When lead dichloride is suspended in hydrochloric acid and gaseous chlorine passed into the liquid, a solution of lead tetrachloride is obtained, from which, on addition of ammonium chloride, a compound, $\text{PbCl}_4 \cdot 2\text{NH}_4\text{Cl}$, analogous to ammonium stannichloride, separates. If this compound is added to concentrated sulphuric acid, an energetic reaction ensues, and lead tetrachloride separates as an oily substance; it is purified by shaking with fresh quantities of sulphuric acid. In the pure state, it is a translucent, yellow, highly refractive liquid which fumes in contact with moist air, with decomposition into lead dichloride and chlorine; it may be kept under cold concentrated sulphuric acid, but when heated with it, it decomposes with explosion into lead dichloride and chlorine. When, however, lead tetrachloride is heated in a retort with concentrated sulphuric acid, and a current of chlorine passed through, a certain quantity of the tetrachloride distils over below 105° , at about which temperature explosion occurs. The sp. gr. of lead tetrachloride at 0° is 3.18, and it solidifies to a yellowish, crystalline mass at -15° ; it forms a hydrate in the presence of a little water, which, by the further addition of water, decomposes into lead peroxide and hydrogen chloride; when brought in contact with a small quantity of cooled hydrochloric acid, a crystalline derivative, probably $\text{PbCl}_4 \cdot 2\text{HCl}$, is formed.

When ammonium stannichloride is added to concentrated sulphuric acid, stannic chloride is precipitated, and may be distilled over. Further details of these and other experiments will appear in the *Monatsheft*. A. R. L.

Ternary Alloys. Part VI. By C. R. A. WRIGHT (*Proc. Roy. Soc.*, **52**, 11—27; compare this vol., ii, 15).—In this paper, the author studies alloys containing aluminium in place of the zinc used in the mixtures previously described. The aluminium employed contained considerable quantities of impurity, chiefly silicon and iron, which found their way almost entirely into the lighter alloy.

In the case of mixtures of aluminium, lead, and tin, the ratio of tin and lead in the heavier alloy, where the difference between the percentages of tin in the two layers is greatest, corresponds nearly with the formula SnPb_3 . At the temperature of experiment, about 800° , the aluminium alloy contained 1.91 per cent. of lead, and the lead alloy 0.07 per cent. of aluminium. The composition at the limiting point was: lead, 19.4; aluminium, 18.0; and tin, 62.6.

For mixtures of bismuth, aluminium, and tin at 650° , the composition at the limiting point was 18.6, 25.6, and 55.8 per cent. of these metals respectively. The bismuth contained 0.28 per cent. of aluminium, and the aluminium alloy 2.02 per cent. of bismuth when no tin was present.

The limiting alloy for aluminium, lead, and silver contained 40 per cent. of lead, 1.75 per cent. of aluminium, and 58.25 per cent. of silver at 870°. No indications of the existence of a compound of aluminium and silver were obtained. At the same temperature, the limiting composition for bismuth-aluminium-silver alloys, was bismuth, 39.5 per cent.; aluminium, 2.25 per cent.; and silver, 58.25 per cent., representing a ratio between bismuth and aluminium near to that indicated by the formula AlBi_2 . J. W.

Basicity and Functions of Manganous acid. By G. ROUSSEAU (*Compt. rend.*, 116, 1060—1062).—In its compounds with barium and strontium, BaO, MnO_2 and SrO, MnO_2 , manganous acid seems to be bibasic, but in the saline oxide, $2\text{MnO}, \text{MnO}_2$, and the calcium compound, $2\text{CaO}, \text{MnO}_2$, it seems to be tetrabasic. The author has made experiments with a view to determine the influence of the alkalinity of the mixture on the composition of the manganites formed in it.

Calcium chloride is fused at an orange-red heat and mixed in successive small quantities with about one-fifth of its weight of precipitated calcium carbonate. When evolution of carbonic anhydride ceases, the temperature is lowered to the melting point of copper, and dried manganous chloride is added. Under these conditions, long needles of the manganite $\text{CaO}, 2\text{MnO}_2$ form rapidly. After heating for an hour, the crucible is raised to an orange-red heat, and the contents well stirred and again heated for 30 or 40 minutes. Short, brilliant, black prisms of the manganite CaO, MnO_2 are thus obtained. This compound dissolves readily in strong hydrochloric acid, but is not attacked by dilute nitric acid, and differs in this respect from the manganite $2\text{CaO}, \text{MnO}_2$. It is formed in mixtures that contain from 3.24 to 2.56 mols. of calcium chloride for each mol. of the oxide. With from 2.0 to 2.5 mols. of the chloride to each mol. of the oxide, mixtures of CaO, MnO_2 and $2\text{CaO}, \text{MnO}_2$, in varying proportions, are obtained. With 1.92 mols. of the chloride to 1 mol. of the oxide, the compound $2\text{CaO}, \text{MnO}_2$ is obtained pure. It follows that the bibasic manganite ceases to be stable when the mixture contains 2 mols. of calcium chloride to 1 mol. of calcium oxide.

If the crucible is covered, the temperature of the surface of the fused mass rises, and needles of the dimanganite are obtained instead of the manganite. The zone of stability of the latter in fact lies between 1000° and 1100°, the dimanganite being formed above and below these limits. It seems, therefore, that calcium manganite undergoes the cycle of changes that characterises other manganites. When strontium manganite, SrO, MnO_2 , is fused with strontium chloride, to which increasing quantities of strontium oxide are added, it changes progressively, and tends towards a limit corresponding with the bibasic manganite, $2\text{SrO}, \text{MnO}_2$.

It would seem that manganous acid is capable of behaving as a tetrabasic acid, but it has really only two acid functions, giving rise to salts of the type $\text{M}''\text{O}, \text{MnO}_2$, whilst the other two functions are more of the nature of alcoholic functions, and are active only in strongly basic media.

The existence of salts such as $2\text{CaO}, \text{MnO}_2$, derived from the unknown hydroxide $\text{Mn}(\text{OH})_4$, affords further evidence that manganese is tetravalent.

C. H. B.

Hydrates of Manganous Sulphate. By C. E. LINEBARGER (*Amer. Chem. J.*, 15, 225—248).—The author describes the methods by which he has obtained manganous sulphate crystallising with 1, 2, 3, 4, 5, 6, and 7 mols. of water, and has determined the solubility of the seven hydrates, and of the anhydrous salt, in water. The salt has the property of uniting with water to form "crystallo-hydrates" between the temperatures -10° and $+117^\circ$; below the former temperature, a mechanical mixture of the heptahydrate and ice separates out; above the latter temperature, only the anhydrous salt is capable of existence. As the amount of water of crystallisation in the hydrates seems in the main to depend on the temperature, this interval of 127° may be divided into seven intervals without any sharp lines of demarcation, to each of which one of the hydrates corresponds. The solubilities of the hexa-, penta-, tetra-, tri-, and di-hydrates do not increase so rapidly as the temperature, whilst the solubilities of the mono-hydrate and of the anhydrous salt diminish less rapidly than the temperature rises. Moreover, considering the hexa-, penta-, tetra-, and tri-hydrates, the more water of crystallisation the hydrate contains, the greater its solubility. The contrary is generally the case with the different hydrates of other salts examined up to date.

The heat of solution of the penta- and tetra-hydrates is undoubtedly negative, whilst their heat of dilution is positive. A solution of the sulphate containing 70 parts of anhydrous salt to 100 parts of water (the concentration of a saturated solution of the tetrahydrate at 20°), when exposed to the temperature of 25° , dissolves more of the tetrahydrate, with a slight absorption of heat, a result entirely in accordance with the law showing the relation of temperature to solubility, advanced by Le Chatelier and Van't Hoff.

G. T. M.

Mineralogical Chemistry.

New Mineral from Boléo, Mexico. By E. CUMENGE (*Compt. rend.*, 116, 898—900).—The copper deposit of Boléo, in Lower California, worked by a French company on a large scale, has already furnished a curious mineral species described in 1891, by Mallard and Cumenge, as boléite. The author has now discovered in the Soledad Valley a new mineral containing, like boléite, copper, lead, and chlorine, but in different proportions. The orthorhombic crystals are of a violet-blue colour, and have a sp. gr. of 4.67. Analysis gave results in accord with the formula $\text{PbCl}_2, \text{CuO} + 2\text{H}_2\text{O}$.

B. H. B.

Metacinnabarite from Idria. By A. SCHRAUF (*Jahrb. f. Min.*, 1893, i, Ref. 461—466; from *Jahrb. k. k. geol. Reichsanstalt*, 41, 379—399).—In this exhaustive memoir, the author gives the results of a series of investigations of rocks and minerals from Idria. The most interesting mineral he describes is the black mercury sulphide, metacinnabarite, found in the Josefi workings at Idria. In a state of purity, this mineral has a sp. gr. of 7·66, and contains 85·62 per cent. of mercury and 14·09 per cent. of sulphur.

B. H. B.

Arsenical Pyrites. By F. SCHERER (*Zeit. Kryst. Min.*, 21, 354—387).—In this monograph on arsenical pyrites, the author gives a full bibliography of the subject, and the results of a crystallographical and chemical examination of arsenical pyrites from the following localities:—1. Freiberg (Himmelfahrt mine); 2. Macagão, Brazil; 3. Deloro, Ontario; 4. Thala Bisztra and Oravicza; 5. Turtmannthal, in Wallis; 6. Modum, in Norway; 7. Bieber, in Hessen; 8. Bräunsdorf, near Freiberg; 9. Munzig, near Meissen; 10. Rauris, in Salzburg; 11. Redruth, in Cornwall; 12. Pestarena, in Piemont; 13. Sala, in Sweden; and 14. Csiklova, in the Banat. Of the last seven, only crystallographical descriptions are given. At the conclusion of the paper, a tabular statement is given of the crystallographic form and chemical composition of all the varieties of arsenical pyrites that have been examined.

The chief conclusions to be drawn from the mass of information got together by the author are, that the arsenical pyrites are frequently not homogeneous compounds, but contain inclusions of magnetite and of other minerals, and that the axial ratio $a : b : c$ does not appear to be dependent on the percentage of sulphur the mineral contains.

B. H. B.

Hauchecornite, a Nickel-bismuth Sulphide. By R. SCHEIBE (*Jahrb. f. Min.*, 1893, i, Ref. 466—467; from *Jahrb. k. preuss. geol. Landesanst. für* 1891, 91—125).—This mineral was found in 1884, in spathic iron ore, at the Friedrich mine, in the mining district of Ham, on the Sieg. Hauchecornite is of a light, bronze-yellow colour, with a hardness of 5, and a sp. gr. of 6·4. On analysis, it yielded—

S.	Bi.	Sb.	As.	Pb.	Zn.	Fe.	Co.	Ni.
22·74	24·10	6·22	1·10	0·22	0·04	0·44	1·45	44·01

Its formula is $\text{Ni}_{14}\text{SbBi}_2\text{S}_{13}$.

B. H. B.

Zirconiferous Felspathic Inclusion in Basalt. By F. GONNARD (*Compt. rend.*, 116, 896—898).—A quarry opened some years ago on the south flank of the Montaudou peak, near Royat, has attracted the attention of geologists, who have examined the felspar inclusions in the basaltic rock. The author now describes a specimen of this felspar, enclosing several very fine zircons of a hyacinth-red colour. This is the first undoubted example of the existence of zircon in its usual matrix that has yet been met with in the Puy-de-Dôme.

B. H. B.

Phosphates from Florida. By H. J. BUISMAN and A. R. VAN LINGE (*Rec. Trav. Chim.*, 286—289).—Four samples of phosphates from Florida have been analysed: I was soft, white, and had not been ignited; II, hard, white, ignited; III, hard, greenish-grey, marbled, ignited; IV, not ignited, otherwise like III.

	I.	II.	III.	IV.
H ₂ O (lost at 150°)....	0·77	0·76	0·63	1·10
CO ₂	1·36	1·67	2·20	2·51
P ₂ O ₅	32·49	36·61	34·99	35·57
Fe ₂ O ₃ + Al ₂ O ₃	2·60	2·65	2·70	1·70
F	3·29	3·40	3·40	3·16

The phosphoric acid, if all combined with calcium, corresponds with

Ca ₃ (PO ₄) ₂	70·92	79·98	76·37	77·64
---	-------	-------	-------	-------

No bromine could be detected, and only traces of chlorine.

C. F. B.

Phosphatic Rocks of Animal Origin and a New Type of Phosphorites. By A. GAUTIER (*Compt. rend.*, 116, 928—933).—The Grotto of Minerva or La Coquille, in the extreme south-west of the Department of Hérault, contains yellowish-white, micro-crystalline *brushite*, CaHPO₄·2H₂O. The floors of the galleries consist of an earthy and concretionary phosphatic deposit of a thickness of at least 7 or 8 metres. This deposit contains flint implements, pottery, bronze ornaments, and other prehistoric remains, together with a large quantity of bones. One of the bones, a dorsal vertebra of a cave bear, had the composition CO₂, 2·264; SO₃, 0·283; P₂O₅, 34·790; Cl, 0·065; F, 0·853; Al₂O₃ (and traces, Fe₂O₃), 0·610; CaO, 44·590; MgO, 0·106; ZnO, 0·149; Pb, traces; silica and sand, 2·163; nitrogenous organic matter, 5·24; water lost at 170°, 8·78 = 99·893. It is noteworthy that the chlorine originally present in the bones has been to a great extent displaced by fluorine. The presence of zinc is probably due to the fact that the animals were fed in a district the soil of which contains zinc.

The deposit in which the bones are embedded varies in composition, but an average sample gave the following numbers on analysis:—Water lost at 120°, 5·81; loss at a red heat, 4·33; sand and ferruginous clay, 45·25; CaSO₄, 11·31; CaCO₃, 4·00; Ca₃(PO₄)₂, 17·45; Al₂P₂O₈, 10·63; CaF₂, 1·83; MgO, trace.

C. H. B.

New Type of Phosphorites. By A. GAUTIER (*Compt. rend.*, 116, 1022—1028).—In the Grotto of Minerva (preceding abstract), at a depth of 3 to 4 metres below the surface, there is a yellowish, hard, concretionary layer, from 5 to 9 metres thick, which follows the undulations of the underlying Devonian rock. This concretionary layer has the composition: water and organic matter, 17·18; SiO₂, 13·00; CaO, 16·24; Al₂O₃, 24·29; P₂O₅, 27·59; Mg, Fe, SO₄, traces; F, 2·104 = 100·404. The other phosphates found in the same deposit differ considerably in composition and in physical properties, some being

brittle, and even pulverulent, and some so light that they float upon the water, but they are alike in containing a considerable proportion of aluminium phosphate and so low a proportion of calcium that it is not sufficient to form tricalcium phosphate, nor even, in some cases, dicalcium phosphate. In this respect the phosphorites of the Grotto of Minerva differ from all ordinary phosphorites, the proportion of calcium in the latter being always sufficient to form tricalcium phosphate. The phosphorites in the grotto also contain a higher proportion of calcium fluoride.

The aluminium and calcium phosphates seem to be simply mixed, since the former dissolves readily in dilute solutions of alkalis, and ammonium citrate dissolves a much larger proportion of phosphoric acid than from ordinary phosphorites.

The only known double phosphates of aluminium and calcium are *tavistockite* and *cirrolite*, but both these are rare, and the deposit in the Grotto of Minerva is the first to yield the two separate phosphates, crystallised dicalcium phosphate and hydrated aluminium phosphate.

C. H. B.

Brandite and Friedelite. By G. LINDSTRÖM (*Jahrb. f. Min.*, 1893, ii, Ref. 9—10; from *Geol. Fören. i Stockholm Förh.*, **13**, 123).—Brandite occurs with heavy spar, calcspar, caryopilite, and sarkinite in fissures in the Harstig mine, Sweden. Analysis gave the following results:—

As ₂ O ₅ .	P ₂ O ₅ .	PbO.	MnO.	FeO.	MgO.	CaO.	H ₂ O.	Cl.
50·48	0·05	0·96	14·03	0·05	0·90	25·07	8·09	0·04

The formula is therefore $2\text{CaO}, \text{MnO}, \text{As}_2\text{O}_5 + 2\text{H}_2\text{O}$. The mineral has a sp. gr. of 3·671. It crystallises in the triclinic system.

Red hexagonal crystals of friedelite are found at the same mine, with galena, specular iron ore, and augite in fissures filled with calcite. On analysis, they yielded the following results:—

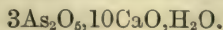
SiO ₂ .	FeO.	MnO.	CaO.	MgO.	Cl.	H ₂ O.	P ₂ O ₅ .
33·36	3·83	49·08	0·74	1·31	4·19	8·45	trace

The percentage of manganese oxide is somewhat too high, on account of admixed hausmannite.

B. H. B.

Adelite and Svabite, New Swedish Minerals. By H. SJÖGREN (*Jahrb. f. Min.*, 1893, ii, Ref. 38—39; from *Geol. Fören. i Stockholm Förh.*, **13**, 781).—A new basic arsenate from Nordmarken and Långban is termed by the author adelite (*ἄδελος*, cloudy). It occurs in large masses with manganese minerals. Analysis gave results in accord with the formula $4\text{RO}, \text{H}_2\text{O}, \text{As}_2\text{O}_5$, in which R represents Ca, Mg, together with some Mn, Fe, Pb, Cu.

Svabite is a new mineral of the apatite group from the Harstig mine. Its composition is represented by the formula



The chemical analogy with apatite is supported by the results of the crystallographical examination.

B. H. B.

Långbanite. By H. SJÖGREN (*Jahrb. f. Min.*, 1893, i, Ref. 471—472; from *Geol. Fören. i Stockholm Förh.*, 13, 256).—The author has continued, on material recently obtained at Långbanshyttan, his former researches, and finds that the hexagonal tablets in finely granular schefferite are composed of långbanite. Analyses of these tablets, and of the columnar crystals, show that the general formula of the mineral is $R_2O_3 + RR'O_3$.

In a subsequent paper (*Geol. Fören. i Stockholm Förh.*, 13, 271), H. Bäckström gives further analyses of this mineral, showing that it is an isomorphous mixture of compounds of the general formula $R^mR^nO_3$ (compare Abstr., 1891, 1436). B. H. B.

Mineral Chemical Studies. By S. J. THUGUTT (*Jahrb. f. Min.*, 1893, ii, Ref. 10—12).—The author has prepared and analysed alteration and substitution products of various minerals by the method successfully adopted by Lemberg, with a view to obtaining information on the constitution of these minerals. His experiments relate to the sodalite group, the formation of kaolin, the alterations of corundum, of diaspore, and of natural glasses, basic sulphates, and sulphoferrites. B. H. B.

Astochite. By H. SJÖGREN (*Jahrb. f. Min.*, 1893, ii, Ref. 37—38; from *Geol. Fören. i Stockholm Förh.*, 13, 604).—Astochite, described by the author as a new member of the amphibole group, occurs in blue aggregates in association with rhodonite at the Långban mine, in Wermland. It crystallises in the monoclinic system, and the results of analysis proved it to be a metasilicate, in which the compounds $(Mg, Mn, Ca)SiO_3$ and $(Na, K, H)_2SiO_3$ occur. The latter silicate has not hitherto been met with in the hornblende series. B. H. B.

Astochite and Dahllite. By A. HAMBERG (*Jahrb. f. Min.*, 1893, ii, Ref. 39—40; from *Geol. Fören. i Stockholm Förh.*, 13, 801).—The author discusses the two alleged new minerals astochite and dahllite. Sjögren's astochite, he shows, is identical with the mineral richterite analysed by Michaelson and Igelström. The mineral described by Brögger and Bäckström as dahllite he regards as identical with stafelitte, a mineral described by Stein, Streng, Petersen, and Sandberger. B. H. B.

Diopase from the Congo. By A. LE CHATELIER (*Compt. rend.*, 116, 894—896).—Some interesting specimens of diopase have been found by the author at the Mindouli copper mines, on the road from Loango to Brazzaville. These mines are worked by the natives on a large scale. At the most important of the four centres of activity there are 150 to 200 shafts, and 300 to 350 natives employed in the extraction of malachite. The diopase occurs in geodes, in quartzite, or in a crystalline rock, shown, on analysis, to consist of a mixture of quartz, willemite, and lead and calcium carbonates. Near the diopase, an amorphous copper silicate is found, resembling chrysocolla, but in composition identical with diopase. The deposit, which

appears to be the capping of a vein not yet discovered, is described in detail by the author, and analyses of the various minerals are given.

B. H. B.

Composition of Helvine. By A. KENGOTT (*Jahrb. f. Min.*, 1893, ii, Mem. 72—74).—The formula deduced from published analyses, by Bäckström and by Rammelsberg, of helvine from Norway is $6(2\text{RO},\text{SiO}_2) + \text{MnS}_2$, whilst that deduced from Teich's analysis of helvine from the Ural is $6(2\text{RO},\text{SiO}_2) + 2\text{MnS}$. Analyses of danalite and of the Ural helvine lead to the latter formula, and it appears desirable that further analyses should be made of the Norwegian helvine, to ascertain whether this mineral also should have the same formula assigned to it.

B. H. B.

The Formula of Tourmaline. By A. KENGOTT (*Jahrb. f. Min.*, 1893, ii, Mem. 71).—In a former paper (Abstr., 1892, 1415), the author showed, by the calculation of a number of analyses, that the whole tourmaline series might be regarded as mixtures, in varying proportions, of two isomorphous substances: A represented by the formula $3\text{R}_2\text{O},\text{SiO}_2 + 5(\text{R}_2\text{O}_3,\text{SiO}_2)$, and B represented by the formula $2(3\text{RO},\text{SiO}_2) + \text{R}_2\text{O}_3,\text{SiO}_2$. A recent analysis, by Katzer, of the tourmaline from Benitz, in Bohemia, affords a confirmation of this theory, the author's calculations showing that it consists of 2 parts of A and 1 of B.

B. H. B.

Synthesis of Minerals. By J. MOROZEWICZ (*Jahrb. f. Min.*, 1893, ii, Mem. 42—51).—The author gives further details of his experiments (this vol., ii, 19) on the synthesis of hauyn, and concludes that minerals of that group may be formed without difficulty from a silicate magma of corresponding composition, if the melting point of such magma is not too high. At high temperatures, these minerals cannot be formed, and, in their place, anorthite and nepheline are produced.

The author also gives the results of some experiments on the formation of quartz, biotite, and sanidine from molten liparite.

B. H. B.

Zeolites from Brazil. By E. HUSSAK (*Zeit. Kryst. Min.*, 21, 405—408).—The author gives a lengthy description of the zeolites from the augite-porphyrite of S. Paulo and Santa Catharina. Heulandite, in fine, large crystals, gave, on analysis, the following results:—

SiO_2	Al_2O_3	CaO	K_2O	Na_2O	H_2O	Total.
58.10	16.67	5.90	3.26	0.61	16.16	100.70

Other analyses given are the following:—

	SiO_2	Al_2O_3	CaO	Na_2O	H_2O	Total.
I.	47.61	26.80	7.08	7.80	12.11	101.40
II.	60.82	16.67	4.25	1.73	18.12	101.59
III.	45.96	26.03	13.53	—	13.67	99.19

I, Mesolite from the Serra de Botucatú; II, desmine from the Serra de Brotas; and III, scolezite from the Serra de Tubarão, in the State of Santa Catharina.
B. H. B.

Meteoric Iron from Augustinovka (Russia). By S. MEUNIER (*Compt. rend.*, 116, 1151—1153).—The meteorite from Augustinovka, Ekaterinoslav, weighs 25 lbs., and is remarkable because it was found in the post-tertiary clay. Examination of some of the partially oxidised external layers shows that the meteorite contains schreibersite, insoluble in hydrochloric acid, but soluble in nitric acid, together with some nickel and phosphoric acid, but mixed, in these altered and oxidised outer layers, with a large proportion of ferric oxide.
C. H. B.

Physiological Chemistry.

Artificial and Natural Digestion. By R. H. CHITTENDEN and G. L. AMERMAN (*J. Physiol.*, 14, 483—508).—Natural digestion is admittedly different from digestion carried out in a flask. It is probably more rapid and more complete, the products of digestion being continually removed and fresh juice poured out. This was well pointed out by S. Lea (*Abstr.*, 1890, 536), who dealt especially with starch. He found that, by carrying out the digestion in a dialyser in constant movement, the intermediate dextrins were found in small amount only, and surmised that, in the body, the conversion into sugar was practically complete. In the present research, it is gastric juice that was the subject of study, and the method adopted was practically the same as in Lea's experiments. This method, although more like natural digestion than that carried out in a flask, is still imperfect, as it is impossible to imitate the vital selective action of the cells of the lining of the stomach and intestines.

It was found that the amount of true peptone, in comparison with albumose, was not markedly different in the dialyser and flask experiments, and the opinion is expressed that the normal action of gastric juice is not to completely peptonise proteid, but rather to act as a preliminary to the more vigorous action of the pancreatic juice. This supposition was confirmed by examining the contents of the human stomach after a meal of egg-white. The amount discovered was small, and it is not easy to say exactly how the loss occurs; doubtless it is partly by absorption through the gastric walls, and partly by onward passage to the duodenum. The fact, however, that peptone and proteose were found an hour or more after the meal shows that absorption from the stomach is not immediate, as has often been taught. The proportion of proteose is always greater than that of peptone.

In the course of the experiments with dialysis, it was noticed that albumoses were discoverable in the dialysate. This was not unex-

pected. On testing this question quantitatively, it was found that the proteoses were diffusible to a considerable extent, but not nearly so much as peptone. A curious fact, which was unexpected, was that deutero-proteose is less diffusible than proto-proteose. Proto-gelatose is fairly diffusible, but it has a somewhat lower endosmotic equivalent than the corresponding proteose. Elevation of temperature increases the rate of osmosis, especially of the proteoses.

W. D. H.

Note by Abstractor.—The greater diffusibility of proto-proteose than that of deutero-proteose has also been noted by Kühne (*Abstr.*, 1893, i, 234).

W. D. H.

Physiology of the Embryonic Heart. By J. W. PICKERING (*J. Physiol.*, 14, 383—466).—Experiments on the hearts of chick embryos, mostly 72 hours old, were performed by exposing the embryo by a hole in the egg shell, and keeping it *in situ* in a water-bath, the upper surface of which was covered by a glass plate. The heart of each embryo has an individual rhythm, which varies directly with the temperature. Extremes of temperature stop the heart in an expanded condition. Caffeine, digitalin, and strophanthin modify the tone of the embryonic heart, and finally stop its ventricle in strong systole.

Strychnine, morphine, veratrine, nicotine, amylic nitrite, and potassium chloride stop the heart in an atonic condition. An antagonism exists between veratrine and potassium chloride, and between nicotine and potassium chloride, in their action on the embryonic heart. Morphine acetate and amylic nitrite in the final phases of their toxic action reverse the rhythm of the embryonic heart. Atropine has only a slight depressant action on the rhythm. Muscarine nitrate has apparently no specific action on the hearts of embryos between the 57th and 96th hours.

Chloroform depresses the heart to stoppage in extreme diastole. Ether primarily stimulates, and in large doses depresses it.

The fact that the heart at this period has no nerves, furnishes a means of distinguishing in the action of drugs those that act on the muscular from those that act on the nervous structures of the heart.

W. D. H.

Proteïds of the Crystalline Lens. By C. T. MÖRNER (*Zeit. physiol. Chem.*, 18, 61—106).—The crystalline lens of the eye yields a certain amount of proteïd matter to water and saline solutions. About 48 per cent. of proteïd remains undissolved. This insoluble substance is termed albumoid, and is most abundant in the inner, denser portions of the lens. It yields no nucleïn on gastric digestion, and the small amount of phosphorus it contains is due to inorganic phosphates. The soluble proteïds of the lens are also not nucleïn compounds. About 2 to 4 per cent. of the soluble proteïd is albumin; the rest is globulin. The globulin is precipitated by saturation with magnesium sulphate, but not by sodium chloride; in this it resembles vitellin. The globulin consists of two proteïds, α -crystallin and β -crystallin.

α -Crystallin is completely precipitable by saturation at 30° with

magnesium sulphate or sodium sulphate; by the addition of $1\frac{1}{2}$ times its volume of saturated ammonium sulphate solution by a stream of carbonic anhydride, and by very dilute acetic or hydrochloric acids. It coagulates at 72° . It contains N, 16.68; S, 0.56; C, 52.83; and H, 6.94 per cent. $[\alpha]_D = -46.9^{\circ}$.

β -Crystallin differs from this in its coagulation temperature (64°). $[\alpha]_D = -43^{\circ}$. It contains 17.04 nitrogen and 1.27 sulphur per cent.

The proportion between these four proteïds is given in the following table:—

	Total proteïds.	Soluble proteïds.	In fresh lens.
Albumoid	48.0 per cent. ..	—	17.0 per cent.
α -Crystallin	19.5 " ..	37 per cent.	6.8 "
β -Crystallin	32.0 " ..	62 " 	11.0 "
Albumin	0.5 " ..	1 " 	0.2 "
Total proteïds	—	—	35.0 "

α -Crystallin is more abundant in the outer, β -crystallin in the inner, portions of the lens; the albumin is equally distributed. The lens contains no keratin.

W. D. H.

Proteïds of Spleen and Thyroid. By F. GOURLAY (*Proc. Physiol. Soc.*, 1893, 8—9).—The proteïds obtainable from the spleen are precipitable from saline solutions by saturation with magnesium sulphate, and therefore fall into the globulin or nucleo-albumin class. The amount of albumin is small. They resemble very closely the proteïds described by Halliburton as obtainable from lymphoid structures. Further, the nucleo-albumin can be prepared either by the acetic acid method of Wooldridge or the sodium chloride method of Halliburton. It causes intravascular coagulation. Spleens were placed under alcohol for some months. The proteïds were entirely coagulated, and no trace of peptone or proteose was discoverable. The opinion is expressed that Schmidt's cytoglobin is nucleo-albumin which had escaped coagulation by insufficiently long exposure to alcohol.

The absence of proteoses and peptone is important in view of Martin's discovery that the albumoses of disease (diphtheria, tetanus, &c.) accumulate in the spleen. Devoto's modification of the ammonium sulphate method was also used with the same negative results. If the spleens are not perfectly fresh, proteoses are discoverable. They are probably formed *post mortem* by a process of self-digestion or putrefaction. v. Jaksch states that normal spleens do contain "peptone"; it is possible that he did not use the perfectly fresh organs.

The proteïds obtainable from the thyroid are very similar. The yield of nucleo-albumin by Wooldridge's method is, however, small; the aqueous extract is rendered cloudy by the addition of weak acetic acid, but there is little or no precipitation. The yield by the sodium chloride method is large. The question then arises, Is some of this derived from the colloïd substance? It appears that it is so, and the

method introduced by Lilienfeld and Monti (this vol., ii, 135) for the localisation of phosphorus led to positive results. The so-called colloïd substance is stained as darkly as, or in some cases more darkly than, the cells. The hypothesis that colloïd substance is not mucin is confirmed by the fact that after boiling thyroids with dilute sulphuric acid, there was no formation of a reducing sugar.

W. D. H.

Action of Physiological Saline Solution on Blood Corpuscles. By H. J. HAMBURGER (*Centralbl. f. Physiol.*, 7, 161—165).—In recently published papers, Bleibtren and others (this vol., ii, 331, 332) have brought forward a method of estimating the volume of the blood corpuscles by analysing mixtures of blood and physiological saline solution (0·6 per cent. sodium chloride solution), on the supposition that this reagent has no influence on the corpuscles.

In the present paper, it is pointed out that this supposition is not borne out by facts. The saline solution has a considerable influence on the volume of the corpuscles; in the ox and pig, the strength of the solution should be 0·9 per cent., which has the same water attracting power as the serum of those animals. But even this is not an indifferent fluid, for it dissolves out a good deal of proteid from the corpuscles, although not so much as physiological salt solution does. The only completely indifferent fluid known is blood serum.

W. D. H.

Coagulation of Blood. By A. E. WRIGHT (*J. Pathol. and Bacteriol.*, 1, 434—450).—A critical account is given of the various theories of blood coagulation. None is absolutely satisfactory, nor applicable to all forms of blood or blood plasma obtained by artificial means. The importance of nucleo-albumin and calcium salts is recognised; the fibrin ferment theory, as taught by Schmidt and Hammarsten, is considered to have little or no substratum of fact.

With regard to the influence of carbonic anhydride, it is suggested that the loss of coagulability of peptone blood may be associated with the impoverishment of the blood in this gas. Peptone plasma is rich in dissolved nucleo-albumins; the white corpuscles having dissolved, or, at least, disappeared, the alkalinity of peptone plasma is reduced; this may be due to the solution of nucleo-albumin, a substance with acid properties, and further the loss of carbonic anhydride may be assumed to be due to the nucleo-albumin driving out the gas from its combination with bases. Peptone plasma gives a heavy precipitate of nucleo-albumin on adding a weak acid, probably because it is thereby dissociated from its combination with bases. This precipitation of nucleo-albumin would place it at the disposal of the plasma for purposes of coagulation.

If this explanation holds true, the coagulation of peptone plasma by carbonic anhydride would be a direct reversal of the driving out of the gas which results from peptone injection, and the phenomena of coagulation in peptone plasma are governed by the same conditions as those of intravascular coagulation after injection of Wooldridge's "tissue fibrinogen." The distribution of coagulation after such injections is determined by the amount of carbonic anhydride which is present in the various vascular areas.

W. D. H.

Iron in Chlorosis. By R. STOCKMAN (*Brit. Med. J.*, 1893, i, 881—885, 942—944).—It is an undoubted fact that iron administered in an inorganic form does good in cases of chlorosis. The present paper dwells on the fact that inorganic iron is the best remedy, the cure being quicker than when iron is given in organic compounds, such as blood or hæmatin; Kobert's (*St. Petersburg Med. Woch.*, 1891) preparations, hæmol and hæmogallol, prepared from blood, although tasteless and unirritating, did not give encouraging results.

The results of the present paper also tend in favour of the theory that iron is absorbed, and does not simply act as a stimulant, or by combining with hydrogen sulphide in the intestines, as Bunge considers. The grounds on which this conclusion is based are—

1. Iron inorganic compounds cure chlorosis when given hypodermically.

2. Sulphide of iron itself cures chlorosis.

3. Bismuth, manganese, and other drugs—which are just as capable as iron of combining with hydrogen sulphide—do not cure chlorosis.

Full details of cases are given.

Why inorganic iron does not increase the hæmoglobin of healthy people is an unsolved problem which is hardly touched in the present research.

W. D. H.

Action of Drugs containing Iron. By C. T. MÖRNER (*Zeit. physiol. Chem.*, 18, 13—20).—Many observers state that inorganic iron salts are not absorbed. The normal supply of iron is hæmatogen, an iron-containing organic compound of the nature of nucleo-albumin. If growing animals are deprived of this, they waste in spite of the administration of inorganic iron. Bunge explains the usefulness of inorganic iron in chlorosis by supposing that the putrefaction processes in the intestines destroy hæmatogen, but that this is protected by the presence of simple iron compounds which leave the body in the fæces as iron sulphide. In chlorosis, also, the normal antiseptic, the hydrochloric acid of the gastric juice, is less than normal. These views of Bunge suggest certain difficulties, and a question here investigated is, Are iron salts antiseptics? The amount of ethereal hydrogen sulphates in the urine is a measure of the amount of putrefactive change in the intestine. By experiments on the author's own person for five periods, two without and three with iron, the proportion of the two classes of urinary sulphates was practically the same (1 : 10·4 for the iron periods, 1 : 10·9 for the other periods). Iron salts are, therefore, not antiseptics; their usefulness rather depends on the readiness with which they form the sulphide and so remove hydrogen sulphide from the alimentary canal.

W. D. H.

Physiological Action of Pentoses. By W. EBSTEIN (*Virchow's Archiv*, 132, 368—369; compare *Abstr.*, 1892, 1506).—M. Cremer (*Sitz. Ges. Morphol. Physiol. München*, 1893, Heft 1) fed starving rabbits on pentoses and found that there was a small increase in the glycogen of their livers. This research on a herbivorous animal does not, however, touch the question formerly investigated by the author, which

was the action of pentoses on the human organism, and the correctness of his results is affirmed. W. D. H.

Abnormal Milk. By W. W. COOKE and J. L. HILLS (*Exper. Stat. Record*, 4, 487; from *Vermont Stat. Rep.*, 1891).—The milk was from a Jersey cow, and the last milking before she went dry. The following results were obtained:—

Total solids.	Fat.	Solids not fat.	Casein and albumin.	Ash.	Milk sugar.
28.43	14.67	13.76	9.98	1.44	2.33

The milk is remarkable for the small amount of milk sugar, the large amounts of proteids and ash, and the very large amount of fat. There seems to be no other record of a milk analysis showing more fat than the solids not fat. N. H. M.

Fœtal Urine. By T. A. HELME (*Brit. Med. J.*, 1893, i, 1261—1262).—The presence of urea in the amniotic fluid has been generally attributed to fœtal urine, but no direct proof that fœtal urine contains urea has hitherto been forthcoming. In the present instance, a small quantity was accidentally obtained during delivery; and the following is the analysis made, comparative experiments being performed with the urine secreted shortly after birth.

The fœtal urine contained no sugar, albumin, phosphates, or sulphates. Urea (0.15 per cent.), creatinine, and chlorides were present. Eight hours after birth, sugar, albumin, and phosphates were absent, but sulphates, chlorides, creatinine (in larger amount), and urea (0.3 per cent.) were present. W. D. H.

β -Hydroxybutyric acid in the Organism. By T. ARAKI (*Zeit. physiol. Chem.*, 18, 1—12).—The appearance of this acid in diabetic urine is not fully understood, but may be partially dependent on insufficient oxidation processes in the organism. The present paper does not, however, work out this aspect of the question, but relates to some of the properties of β -hydroxybutyric acid.

By distillation of an aqueous solution of the acid, a small quantity of crotonic acid is obtained. On subjecting it to putrefaction, crotonic acid, acetic, and probably other fatty acids are obtained, in addition to methane and carbonic anhydride. Administered to animals (rabbits, dogs, frogs), their urine gives the tests in many cases for acetone and acetoacetic acid if oxidation processes in the organism are diminished simultaneously by carbonic oxide poisoning. This result lends support to Minkowski's (*Arch. exp. Path. Pharm.*, 18, 42) theory that these substances in diabetic urine originate from β -hydroxybutyric acid. W. D. H.

Formation of Uric Acid. By G. SALOMON (*Virchow's Archiv*, 132, 370).—In relation to Horbaczewski's work on uric acid (*Abstr.*, 1892, 646), the author advances a claim for priority. W. D. H.

Urobilin. By F. GRIMM (*Virchow's Archiv*, 132, 246—289).—In the fasting condition, normal urine contains no urobilin. At the conclusion of gastric digestion, a larger or smaller quantity appears. Any great amount of the pigment is, however, a pathological condition, the most important cause being the circulation of unorganised blood pigment in the vessels, as after a hæmatoma. In nephritis, it also occurs.

A large number of cases illustrating the presence of urobilinuria in various diseases are given fully. W. D. H.

Mucin Granules of Myxine. By E. W. REID (*J. Physiol.*, 14, 340—346).—The mucus of the hag fish (*Myxine glutinosa*) is secreted in the form of granules peculiar for their size (2 to 5 μ) and flattened oval shape. These granules are produced in mucous cells developed in the slime glands. A solution of the substance of which they are composed presents most of the features of a mucin, but differs from it in not yielding a reducing sugar after prolonged boiling with dilute sulphuric acid. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Nitrogen-fixing Micro-organisms. By BERTHELOT (*Compt. rend.*, 116, 842—849).—Various nutritive matters, such as humic acid, Cohn's liquid, kaolin with humic acid, sugar, &c., were inoculated with soil organisms and the bacteria from leguminous roots, &c., and the gain of nitrogen, if any, determined. The experiments were conducted in flasks of 600 c.c. to 6 litres capacity.

I. *Experiments with Soil Organisms.*—The following experiments were made: (1) mixed soil bacteria in humic acid, in humic acid and kaolin, and in kaolin; (2) a bacillus isolated from soil in humic acid and in Cohn's liquid; (3) check experiment, not inoculated; (4, 5, and 6) three different soil bacilli, each in various nutritive media. The results showed a considerable gain of nitrogen where the mixed bacteria were employed, and also in experiments 2 and 5, whilst in the check experiment and in Nos. 4 and 6 there was practically no gain of nitrogen.

II. *Experiments with Leguminous Root Bacteria.*—The bacteria were obtained from lupin roots which had nodules. The two experiments lasted about four months, and each showed a gain of 50 per cent. of the initial nitrogen.

III. *Experiments with Aspergillus niger.*—The experiments made with pure cultures of *Aspergillus niger* showed a gain of 18—37 per cent. nitrogen; a check experiment with Cohn's liquid and tartaric acid, not seeded, showed no sign of nitrogen. It was noticed that the tartaric acid employed was largely consumed or destroyed under the influence of *Aspergillus niger*.

IV. *Experiments with Alternaria tenuis*.—The cultivations were pure and developed well. The nitrogen fixed amounted to 36, 49, 50, and 98 per cent. respectively of the initial amounts.

There are, therefore, non-chlorophyllous micro-organisms of very different character which have the power of fixing nitrogen. These organisms do not seem to be able to be sustained by the carbon and hydrogen resulting from the decomposition of carbonic anhydride and water, but require organic carbon and hydrogen in such a form as sugar and tartaric acid, &c. It seems also necessary that nitrogen should be present in the nutritive matter in order to give the minimum vitality indispensable for the fixation of free nitrogen. On the other hand, when the amount of combined nitrogen present becomes large, the organisms prefer to utilise it rather than to fix free nitrogen, and will develop more luxuriantly than when they have to depend on uncombined nitrogen. It is this that limits the fixation of elementary nitrogen in soils (compare *Ann. Chim. Phys.* [6], 14, 487).

The carbonaceous matter of soils would disappear more or less quickly if not regenerated by chlorophyllous plants. The agents which bring about nitrogen fixation and carbon fixation may live independently of each other or may be associated by symbiosis, as in the case of the Leguminosæ. In any case, the fixation of nitrogen does not take place in the higher plants, but in certain lower micro-organisms present in soil.

N. H. M.

Pentosans in Plants. By G. DE CHALMOT (*Amer. Chem. J.*, 15, 276—285).—Pentosans decrease in the seeds of peas and corn (*Zea Mâis*, L.) during the germination, but appear again in the roots and stems; they are therefore transferred. The total amount of pentosans, however, increases during the germination. The amount of cellulose pentosans also increases, but in the case of peas the difference is only very slight.

G. T. M.

Products of Cassava. By E. E. EWELL and H. W. WILEY (*Amer. Chem. J.*, 15, 285—289).—The authors have extended their work, an account of which was published four years ago (*Wiley, Agric. Science*, 2, No. 10, pp. 256, *et seq.*). They find that the root of *Jatropha manihot* or Aipi contains very little mineral matter, 0.5 per cent. in the fresh root, and that the plant is, therefore, one which seems particularly well suited to feed almost exclusively from the air and water. As it requires the minimum of fertilisation, it can be recommended for sandy soils.

G. T. M.

Amount of Starch in different Varieties of Potatoes. By A. PETERMANN (*Bied. Centr.*, 22, 263—266; from *Bull. Stat. Agron. Gembloux*, 1892, No. 51).—The average minimum and maximum percentages of starch found in a large number of different kinds of potatoes examined in 1889, 1890, and 1891, were as follows:—

	1889.	1890.	1891.
Maximum.....	9.8	9.4	11.1
Minimum.....	24.0	26.1	23.3
Average	15.2	16.5	16.6

A table is given, showing the amount of starch, the power of resistance to disease, and the properties of 50 varieties of potatoes. The results of the investigation show that it is possible to produce potatoes which give large crops and at the same time contain a high percentage of starch.

N. H. M.

Reserve Proteïd of the Asparagus Root. By S. H. VINES and J. R. GREEN (*Proc. Roy. Soc.*, 52, 130—132).—The watery extract of asparagus root contains a proteïd which is slightly precipitated from solution by sodium chloride, and completely by ammonium sulphate. Besides this, which is the only proteïd present, there exist in the solution a substance which is precipitated by sodium chloride, a substance precipitated by alcohol from the solution from which the proteïd has been removed, and a substance soluble in alcohol, which gives the xanthoproteïc reaction.

J. W.

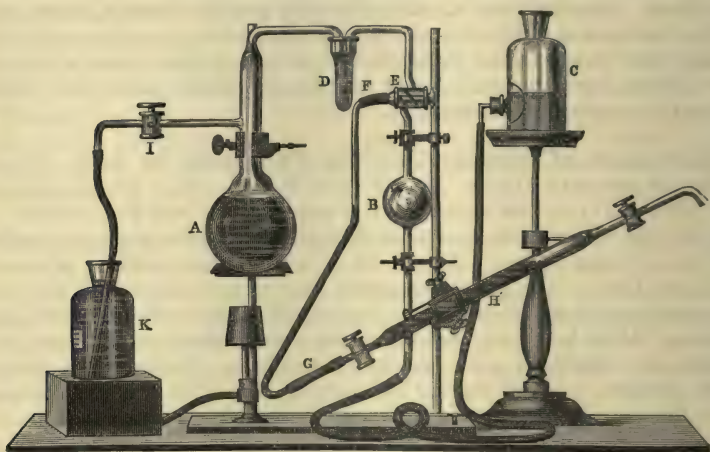
Reversion of Soluble Calcium Phosphate in Soil. By M. STAHL-SCHROEDER (*Exper. Stat. Record*, 4, 587—589; from *J. Landw.*, 40, 213—221).—The object of the experiments was to ascertain the rapidity of the reversion of superphosphate, in concentrated solution, to the di- and tri-basic forms, when mixed with chalk or with soils poor in lime. The superphosphate was mixed with chalk and with clay and arable soil respectively, and made into a thick paste with water. After being exposed in dishes during the desired number of hours, the mixtures were washed into flasks, diluted to a definite bulk, shaken, and left during two hours. A portion was then filtered, and the soluble phosphoric acid, and that soluble in citrate solution, determined. When chalk was employed, the reversion was extremely rapid, but with the two soils only a little more than half the phosphoric acid became insoluble in 20 days. The results indicate that with liberal applications of superphosphate on sandy soils poor in lime, a part of the phosphoric acid may be lost in drainage. Clay soils are likely to lose less. In sandy soils, the application of precipitated phosphate of lime, basic slag, or phosphorite meal is recommended. Composting of the latter with peat and potassium sulphate would be very advantageous, inasmuch as the potassium salts in conjunction with the vegetable acids of the peat would gradually render the phosphoric acid available, and, at the same time, the vegetable matter would improve the water-holding capacity of the soil.

N. H. M.

Analytical Chemistry.

Apparatus for extracting the Gases dissolved in Water.

By G. J. W. BREMER (*Rec. Trav. Chim.*, 11, 278—283).—A is a flask of about 600 c.c. capacity, which contains the water to be examined, EBC is a mercury pump, and FGH the tube in which the gases are collected. The pump is worked by alternately lowering and raising the mercury reservoir C, the stopcock E being so manipulated that the air, or, in the actual experiment, the gases to be examined, is first aspirated into B (capacity 135 c.c.), and then driven out through F. The joint D, connecting the pump with A, consists of a short



tube with an indiarubber cork, through which the two tubes pass; some mercury is placed over the cork to ensure that the joint is airtight. In the experiment, A is partially exhausted, either with an ordinary pump, or by placing some water in it, and boiling, so that the steam drives out the air through I, the stopcock E being closed. Water is then suffered to rise in the tube as far as I, and the vacuum is completed by means of the pump EBC. The vessel K (about 500 c.c. capacity) is now completely filled with the water to be examined; by opening the stopcock I, this water is admitted into A in successive portions; after each addition, the water in A is boiled, and the gases evolved are aspirated into FGH by means of the pump. K is not quite emptied, and the amount of water actually used in the experiment, is determined by finding how much water is required to refill K. The experiment occupies half-an-hour. C. F. B.

Bottle for taking Samples of Water at known Depths. By G. J. W. BREMER (*Rec. Trav. Chim.*, 11, 284—285).—The bottle

stands in a zinc tray, which is weighted with lead, and joined by copper wires to a ring round the neck of the bottle; to this ring is attached the string used for lowering the whole. The bottle is provided with an indiarubber cork, through which pass two tubes, one ending just under the cork, the other reaching to the bottom of the bottle. The upper ends of these tubes project somewhat above the cork, and are slightly enlarged; they are plugged by inserting into them the two ends of a short piece of indiarubber tubing, into which ends short pieces of glass-rod have been pushed. To the top of the indiarubber loop thus formed a string is attached; this is pulled when the bottle has reached the desired depth, the plugs are thus removed from the two tubes, and the water enters the bottle by the longer of the tubes, the air escaping by the other. C. F. B.

Sjöqvist's Method of estimating the Free Hydrochloric Acid in Gastric Juice. By S. BONDZYŃSKI (*Zeit. anal. Chem.*, **32**, 296—302).—The method consists in evaporating gastric juice with excess of barium carbonate, incinerating the residue and determining the barium which has become soluble in the form of chloride. Barium chloride bears, without noteworthy decomposition, ignition at a higher temperature and for a longer time than are required for the incineration, but when mixed with organic substances containing phosphorus and sulphur, a portion of the barium is rendered insoluble in the form of phosphate and sulphate. The addition of barium acetate obviates this source of error, and the estimation may be made in the following manner:—1 gram of barium carbonate is dissolved in acetic acid in a platinum basin, and the solution evaporated to dryness; 25 c.c. of the filtered gastric juice, together with more barium carbonate, are added, the mixture is dried and incinerated to a grey ash. The soluble matters are filtered, and, after adding 25 c.c. of N/10 sodium carbonate, are made up to 125 c.c. The excess of soda in 100 c.c. is then titrated. Then, a being the number of c.c. of soda found, $(20 - a)5$ gives the amount of free hydrochloric acid in 100 c.c. of the gastric juice, expressed in c.c. of N/10 acid.

M. J. S.

A Source of Error in the Volumetric Estimation of Chlorides by Mohr's Method. By W. G. YOUNG (*Analyst*, **18**, 125—129).—The author has found that when estimating chlorine in samples of water without previous concentration, the results obtained are considerably in excess, and they are worse still if the temperature during titration is somewhat high. This is caused by the slight solubility of silver chromate, which requires for every 6 parts 100,000 parts of water at 15.5°, and only one-third of this amount at 100°.

In estimating small quantities of chlorides, it is therefore advisable to evaporate almost to dryness before titration, and to prevent over-dilution, the standard silver should not be too weak.

L. DE K.

Estimation of Sulphur in Organic Liquids. By R. HÖLAND (*Chem. Zeit.*, **17**, 99—100; 130—131).—The accurate estimation of small quantities of sulphur in substances such as tar oils, &c., is still a matter of some difficulty. The author has, however, obtained satis-

factory results by burning the sample in a combustion tube with a mixture of 5 parts of barium carbonate and 1 part of potassium chlorate. The details are practically those of an ordinary combustion, the substance being, however, not inclosed in glass bulbs, but dropped straight on to the back part of the mixture from a 3 c.c. weighed pipette.

The contents of the tube are afterwards digested in dilute hydrochloric acid, and any barium sulphate is then collected and weighed.

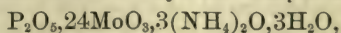
L. DE K.

Estimation of Nitrogen in Nitrates. By T. F. SCHMITT (*Chem. Zeit.*, 17, 173).—The author has slightly modified his process. 10 grams of the sample is dissolved in 500 c.c. of water. 10 c.c. of glacial acetic acid and 10 grams of a mixture of equal parts of iron and zinc powder are put into a 750 c.c. round-bottomed flask, and 25 c.c. of the nitrate solution added from a slow-running pipette. After 10 minutes, when no more gas is evolved, 200 c.c. of water and 30 c.c. of aqueous soda (sp. gr. 1.25) are added and the ammonia is distilled off as usual.

To estimate the total nitrogen in nitrated manures, the author first reduces the substance with the acetic acid mixture, and then boils with excess of sulphuric acid in order also to convert the nitrogenous matter into ammonia.

L. DE K.

Estimation of Phosphoric acid. By A. VILLIERS and F. BORG (*Compt. rend.*, 116, 989—993).—In the complete absence of iron, aluminium, silica, and reducing agents, phosphorus can be accurately estimated in the following manner. The liquid is mixed with about 100 c.c. of the reagent (prepared by dissolving 150 grams of ammonium molybdate in 1 litre of water and pouring this solution into an equal volume of nitric acid of sp. gr. 1.2) for every 0.1 gram of phosphoric acid present. In order to obtain a precipitate that settles rapidly, the reagent should be poured down the sides of the vessel containing the cold solution, and the liquid should not be agitated until after two hours. Potassium compounds and other salts retard the formation of the precipitate, but after heating for four hours at about 40° precipitation is complete. The temperature of 40° should not be exceeded, and digestion should not be prolonged beyond four hours, otherwise the product will be impure. The precipitate is washed with water containing 20 per cent. by volume of the reagent, is collected on a dried and weighed filter, and dried at 100° for six hours. Thus obtained it has always the composition



and 1 part contains 0.03728 part of phosphoric anhydride, P_2O_5 .

In presence of aluminium and iron, the precipitate contains a notable proportion of these metals, which also find their way into the ammonium magnesium phosphate produced from it in the usual way. The following plan, however, leads to exact results:—The precipitate is dissolved in ammonia, mixed with tartaric acid, made slightly alkaline with ammonia, and precipitated with magnesia mixture. The iron and aluminium remain in solution.

C. H. B.

Estimation of Boron. By H. MOISSAN (*Compt. rend.*, 116, 1087—1091).—The boron compound is first converted into boric acid or a borate by the action of nitric acid, and then into methylic borate by distillation with methyl alcohol, as in Gooch's method. The apparatus consists of a small flask with a long neck, provided with a side tube and fitted with a glass stopper carrying a funnel with a stopcock. The side tube is connected with a vertical serpentine condenser, the lower end of which passes into a conical flask through a cork that also carries an exit tube to which is attached a set of bulbs containing dilute ammonia, in order to retain the whole of the methylic borate. A calcium chloride bath, heated by a Bunsen burner, is so arranged that it can readily be applied or removed from the distilling flask.

The substance is placed in the distilling flask, mixed with 1 c.c. of concentrated nitric acid, and distilled to dryness. It is then mixed with 10 c.c. of methyl alcohol, attached to the condensing apparatus, and again distilled. The operation is repeated four times, care being taken to distil to dryness every time before adding a fresh quantity of alcohol. 1 c.c. of water and 1 c.c. of nitric acid are then introduced into the apparatus, distilled as before, and the residue subjected to three more distillations with alcohol. In order to ascertain if all the boron has been expelled, a drop of the alcohol from the end of the condenser is ignited. If there is any green tinge in the flame, the residue in the flask must be again treated with nitric acid and again distilled with methyl alcohol.

A quantity of calcium oxide is strongly heated in a platinum crucible and weighed. The lime is carefully slaked and the distillate is added, taking care to avoid rise of temperature, and allowed to remain for 15 minutes. After ascertaining that the calcium oxide is in excess, the liquid is evaporated at a temperature below the boiling point of methyl alcohol, and the residue is strongly heated and again weighed. The increase in weight gives the quantity of boric anhydride.

The calcium oxide is most conveniently prepared by heating calcium nitrate in such a manner as to form a basic nitrate, which is easy to keep and which is converted into oxide by strongly heating when required.

The results obtained by this method are usually a little low; in the examples given the error varies from -0.27 to -0.4 per cent. of the boric anhydride present.

C. H. B.

Estimation of Silicon in Pig Iron. By H. RUBRICIUS (*Chem. Zeit.*, 17, 101).—The author recommends the following simple process:—5 grams of the finely-divided sample is dissolved in 25—30 c.c. of hydrochloric acid (sp. gr. 1.15) with the aid of a gentle heat. When the metal has dissolved, the solution is diluted to about 150—200 c.c. and filtered. The insoluble matter is washed first with hot water, then with dilute hydrochloric acid (1 : 2), and then again with hot water. The filter, after drying, is put into a platinum crucible and heated until the paper is charred. The crucible is now ignited over the blowpipe, nitre being from time to time added until the carbon

has completely disappeared. 30 grams of ammonium chloride, which must be completely soluble, is now put into a large porcelain basin and dissolved in 75 c.c. of boiling water. The platinum crucible, with its lid, is put into this solution and the whole is boiled for some time. The action of the ammonium chloride on the alkali silicate causes the rapid and complete separation of hydrated silicic acid, which is collected on a filter and washed first with a dilute solution of ammonium chloride and then with boiling water. It is then ignited and weighed.

The test analyses are satisfactory.

L. DE K.

Estimation of Potassium by the Lindo-Gladding Process. By T. BREYER and H. SCHWEITZER (*Chem. Zeit.*, 17, 101—102).—The authors, in reply to Holleman (compare this vol., ii, 344), state that this process has also been investigated by Herff. The results, communicated to the American Association of Official Agricultural Chemists, fully confirm those previously obtained by the authors; not only do they not agree among themselves, but they are, as a rule, from 0.5 to 1 per cent. higher than those obtained by the Stassfurt method. The authors once more recommend that the Lindo-Gladding process should be abandoned.

L. DE K.

Estimation of Alkalis in Silicates. By A. H. LOW (*Chem. News*, 67, 185).—The following scheme is suggested for estimating alkalis in silicates:—1 gram of the finely powdered silicate is decomposed by warming gently with pure, strong hydrofluoric acid and a little sulphuric acid; it is then evaporated to dryness, cooled, mixed with a little aqueous ammonia, boiled, filtered, and washed with a little hot water. The filtrate is rendered strongly acid with hydrochloric acid, the least possible excess of barium chloride added, and the whole boiled and filtered, washing with hot water. This filtrate is then evaporated and gently ignited to expel ammonium salts, and, when cool, treated with ammonium carbonate and aqueous ammonia, boiled, and filtered, washing with hot water. The filtrate is evaporated to dryness in a tared platinum dish and weighed; this gives the mixed chlorides, which are separated in the usual manner.

D. A. L.

Separation of Barium, Strontium, and Calcium. By R. FRESENIUS (*Zeit. anal. Chem.*, 32, 312—317).—The following qualitative method permits the detection of small amounts of any one of the alkaline earths in presence of large quantities of the others. The carbonates are converted into nitrates and thoroughly dried at 180°, and, as soon as cold, triturated with equal volumes of absolute alcohol and ether, any residue being washed with the same mixture. Traces of strontium may pass into solution with the calcium, whilst traces of calcium may remain in the residue. To the solution, 2 drops of dilute sulphuric acid is added. Any considerable precipitate is undoubtedly calcium sulphate. A trifling precipitate may be due to strontium. In this case, 4 c.c. of water is added, and the ether-alcohol evaporated off. A few drops of ammonia are added, with 1 gram of ammonium sulphate, and the liquid is boiled and filtered, acidified

with acetic acid, and tested for calcium by ammonium oxalate. The nitrates insoluble in ether-alcohol are dissolved in 100 c.c. of water, acidified with 3 or 4 drops of acetic acid, heated to boiling, and treated gradually with potassium chromate until the solution is yellow and no longer gives an odour of acetic acid on boiling. After an hour, the barium chromate is filtered off, and a portion of the filtrate tested with ammonia and ammonium carbonate. If a bulky precipitate is produced, it must be strontium carbonate. If otherwise, the rest of the filtrate, mixed with a drop of nitric acid, is concentrated and precipitated with ammonium carbonate, any trifling precipitate is washed, converted into chloride, dried, dissolved in a mixture of 3 vols. of water and 1 vol. of alcohol, and boiled after adding 1 drop of potassium chromate. Strontium is indicated by a pulverulent, yellow precipitate.

For quantitative purposes, either the calcium may first be separated by treating the nitrates with ether-alcohol, and then the barium be separated from the strontium by potassium chromate, or the barium may first be separated as chromate, the calcium and strontium be precipitated as carbonates, converted into nitrates, and separated by ether-alcohol (Abstr., 1891, 110; this vol., ii, 301). Both methods give equally accurate results; the barium and calcium precipitates are pure, the strontium alone retaining a trace of calcium.

M. J. S.

Quantitative Separation of the Metals of the Hydrogen Sulphide Group by means of Bromine Vapour. By P. JANNASCH and W. REMMLER (*Ber.*, 26, 1422—1425; compare Abstr., 1892, 384, 540, 754).—Lead may be separated from tin (and from antimony) by treating the mixed sulphides as described in Abstr., 1892, 384; tin bromide volatilises, whilst lead bromide remains behind. The latter is converted into chloride by treatment with chlorine water, and then into sulphate, in which form it is weighed; the tin is converted into the oxide by repeated evaporation with nitric acid, and so weighed. Results good.

An attempt was made to improve the method by avoiding the precipitation with hydrogen sulphide. This was accomplished by mixing the material to be analysed with 6 to 10 times its weight of sulphur, and heating the mixture in a stream of dry hydrogen sulphide in a glass vessel shaped somewhat like a Liebig's drying tube; the metals remained behind as sulphides, and the excess of sulphur volatilised. The sulphides were then treated, in the same vessel, with bromine vapour as before described; good results were in general obtained. But it was found that metallic tin and tin oxide are only partially converted into sulphide by the above treatment, and the method consequently fails; if, however, 10 to 15 per cent. of iodine is added to the sulphur used, the tin is readily and completely converted into sulphide, and excellent analytical results are obtained.

C. F. B.

Estimation of Lead. By A. H. Low (*Chem. News*, 67, 178—179).—1 gram of ore is heated carefully with 10 c.c. of a mixture of equal parts of nitric acid and water until pretty well decomposed;

the nitric acid is then expelled by boiling with 10 c.c. of concentrated sulphuric acid, and, when cool, 10 c.c. of pure dilute sulphuric acid (1 : 9) and about 2 grams of Rochelle salt are added. When the latter is dissolved, 40 c.c. of distilled water is added, the whole boiled, the precipitate collected, washed with dilute sulphuric acid, and then heated with a saturated solution of ammonium chloride until all the lead sulphate is dissolved; the liquid is then filtered. Strips of pure aluminium are placed in the filtrate, which is boiled until the lead is all precipitated, cold water is added, the lead adhering to the aluminium removed, all the lead collected in a porcelain dish, washed with water, and finally with alcohol, then dried and weighed. A deduction of 3 per cent. is a fair allowance for arriving at the fire assay of a pure ore of the same grade. D. A. L.

Detection of Mercury in Urine. By S. BONDZYŃSKI (*Zeit. anal. Chem.*, 32, 302—303).—In Ludwig's method, the mercury is precipitated from the urine by zinc powder, and then volatilised in a glass tube. Commercial zinc powder, however, contains cadmium, from which it cannot be freed completely even by prolonged and intense ignition in a stream of hydrogen. Nevertheless, even after ignition, it will, when only moderately heated in a tube, give off enough cadmium to form a mirror closely resembling mercury in appearance. Confirmation by means of iodine should, therefore, never be omitted; but it is safer to abandon the use of zinc, and to employ copper, in the form of powder, foil, or turnings.

M. J. S.

Estimation of Manganese in Ores. By A. H. Low (*Chem. News*, 67, 162).—0.5 gram of ore is decomposed with 5 to 10 c.c. of hydrochloric acid or *aqua regia*, and most of the excess of acid is boiled off; the rest, after diluting the solution with 75 c.c. of hot water, is neutralised by boiling with excess of zinc oxide. A saturated solution of bromine is then added in excess, the superfluous bromine being expelled by heating; an excess of zinc oxide should, however, still remain. The precipitate is collected, washed with hot water, treated in a flask with 50 c.c. of dilute sulphuric acid (1 : 9), and dissolved by heating with excess of a standardised solution of oxalic acid, containing about 11.46 grams of acid per litre, and of which 1 c.c. corresponds with about 1 per cent. of manganese; after diluting with hot water, the excess of oxalic acid is titrated with standardised, approximately N/10 potassium permanganate. The amount of oxalic acid consumed by the manganic oxide is thus ascertained, and from it the percentage of manganese is readily calculated. The oxalic acid may be replaced by other reducing agents. D. A. L.

The Thiocyanate Test for Iron. By H. SCHULZE (*Chem. Zeit.*, 17, 2).—The author has noticed that dilute solutions of ferric salts, containing no excess of mineral acids, fail, after some time, to give the characteristic red colour with a thiocyanate. The same happens with concentrated solutions on boiling. The probable cause of this is the conversion of the iron into Graham's soluble ferric hydroxide.

On addition of hydrochloric acid, the normal iron salt will be restored, and the test will be successful. L. DE K.

Estimation of Iron by an Iodometric Method. By E. NIHOUL (*Chem. News*, **67**, 196—198).—Ferric salts or ores containing iron in a ferric state are placed in a distillation flask provided with a tubulated stopper carrying a tube bifurcated above; the salt or ore is dissolved in hydrochloric acid by the aid of heat and the use of gaseous hydrogen chloride if required; a current of carbonic anhydride is then passed and continued throughout the operation; when all the air has been replaced, a slight excess of a strong solution of potassium iodide is introduced through the tube, and the contents of the flask are boiled; when most of the iodine has volatilised, gaseous hydrogen chloride is passed in; this not only ensures the volatilisation of all the iodine, owing to the decomposition of any potassium iodide which would otherwise hold some iodine back, but also the hydriodic acid formed aids the solution of ores, and, in fact, in some cases the potassium iodide may be added partly or wholly at the commencement of the operation, or a mixture of hydriodic and hydrochloric acids may be used in the first instance, taking care, of course, that all the air has been expelled. The distillate is received in a Volhard condenser, containing a solution of potassium iodide, and the iodine is estimated by sodium thiosulphate. Ferrous salts are oxidised in the flask before connecting up the condenser. Any free iodine in the hydriodic acid must, of course, be got rid of before using this acid for the purpose indicated. D. A. L.

Detection and Estimation of Formaldehyde. By A. TRILLAT (*Compt. rend.*, **116**, 891—894).—The liquid to be tested is mixed with a small quantity of dimethylaniline, acidified with sulphuric acid, and agitated briskly. It is then heated on a water-bath for half an hour. The product is made alkaline with sodium hydroxide, boiled until all odour of dimethylaniline disappears, and filtered. The filter-paper is then spread out on a porcelain dish, moistened with acetic acid, and some fragments of finely-powdered lead peroxide scattered upon it. In presence of formaldehyde, a deep-blue coloration appears, due to the formation of the hydrol of tetramethyldiamidodiphenylmethane.

When the solution to be tested is mixed with an equal volume of a neutral solution of 3 grams of aniline in a litre of water, a white cloud, due to the formation of anhydroformaldehydeaniline, appears after several hours. This reaction will detect 1 part in 20,000, but it is also given by acetaldehyde.

The detection of formaldehyde in foods, &c., is often impossible on account of the formation of compounds with various organic substances present in the food.

Formaldehyde can be estimated by weighing it as anhydroformaldehydeaniline, but the results, although strictly comparable amongst themselves, are not absolutely accurate.

Another method is based on the conversion of formaldehyde into hexamethyleneamine by the action of ammonia. The acidity of the solution is first determined by means of sodium hydroxide solution

and phenolphthaleïn; 10 c.c. is diluted with water and mixed with a measured excess of ammonia solution of known strength. A current of steam is then passed into the liquid, and the expelled ammonia is collected and estimated by means of standard acid. The difference between the quantity volatilised and the quantity originally added is the amount required to convert the formaldehyde into hexamethyleneamine. A little of the latter is volatilised in the process.

C. H. B.

Estimation of Salicylic acid in presence of Phenols. By A. FAJANS (*Chem. Zeit.*, 17, 69).—The colorimetric estimation of salicylic acid by means of ferric chloride cannot be carried out in aqueous solutions in the presence of phenols, but advantage may be taken of the fact that the latter give no coloration with ferric chloride in alcoholic solution. To estimate salicylic acid, the suspected liquid is acidified and extracted with ether, which is then allowed to evaporate. The residue is dissolved in 25—30 c.c. of absolute alcohol, introduced into a graduated tube, and mixed with a few drops of a 5 per cent. alcoholic solution of ferric chloride until the colour does not get any darker. In a similar tube, the same amount of an alcoholic solution of salicylic acid (2 : 10,000) is introduced, and then a sufficiency of ferric chloride solution. Finally, the darker of the two mixtures is diluted with absolute alcohol until they both show the same intensity of colour; the difference in volume is noticed, and the amount of salicylic acid is found by a simple calculation. Even in a mixture of 800 parts of phenol and 1 part of salicylic acid, the latter may be estimated with great accuracy.

L. DE K.

Detection and Approximate Estimation of Cotton-seed Oil in Lard and Olive Oil. By F. GANTTER (*Zeit. anal. Chem.*, 32, 303—308).—The author has obtained specimens of cotton oil, as well as of adulterated lard, which give no reaction with Becchi's silver nitrate test; this test can therefore no longer be depended on for the detection of this adulterant. The iodine absorptions of lard and cotton oil, 23—27 per cent. and 43—45 per cent. respectively, as determined by the author's process (this vol., ii, 309), differ widely enough to allow of the calculation, within 10 per cent., of the proportion of cotton oil present. To detect smaller amounts than 10 per cent., 1 c.c. of the perfectly dry, melted fat or oil is dissolved in 10 c.c. of light petroleum in a test tube, a single drop of concentrated sulphuric acid is added, and the whole well shaken. Pure lard gives only a straw-yellow to feeble reddish-yellow coloured liquid, from which, on repose, dark reddish-yellow drops slowly settle out, leaving a nearly or perfectly colourless upper liquor. Olive oil acquires a rather darker colour at first, but behaves like lard on standing. In presence of cotton oil, a deep brown to black colour is immediately produced, and remains unchanged even on standing for a long time. As little as 1 per cent. can thus be detected.

M. J. S.

General and Physical Chemistry.

Influence of Frictional Electricity on the Formation of Amalgams. By G. STAATS (*Ber.*, 26, 1796—1797).—If plates of silver in contact with mercury be subjected to the discharge from an electrical machine, the quantity of amalgam produced in a given time is increased threefold.
H. G. C.

Electrolysis of Alkali Salts. By S. ARRHENIUS (*Zeit. physikal. Chem.*, 11, 805—828).—The author has made experiments which show that when the aqueous solution of an alkali salt is electrolysed with a mercury cathode, a considerable time elapses from the beginning of the electrolysis before hydrogen makes its appearance. This observation proves that hydrogen is not a primary product of the electrolysis, but results from the action of the water of the solution on the alkali amalgam primarily formed by the discharge of the positive ion (the alkali metal). The time necessary for the appearance of the first bubble of hydrogen increases very slowly with diminution of the current strength, and (with a constant current of 0.05 amp.) increases with increase of concentration and lowering of temperature. It is practically constant for equivalent solutions of electrolytes with the same positive ion, but much larger for potassium salts than for lithium and sodium salts.

A theoretical investigation of this phenomenon shows that the electromotive force necessary for electrolysis increases at the beginning with the quantity of electrolytic products already separated. In general, however, secondary reactions occur, which prevent the continued accumulation of these products if the primary process goes on very slowly: in this case the electromotive force necessary for electrolysis is almost exclusively conditioned by these secondary reactions. If the result of the secondary processes is the same as it is in the case of alkali salts, then the E.M.F. necessary for the decomposition will also be the same, or nearly so. This conclusion is in accordance with the experiments of Le Blanc (*Zeit. physikal. Chem.*, 8, 314), which therefore do not necessitate the assumption of a primary decomposition of the water.

From the observation of Shields (this vol., ii, 449) that a decinormal solution of sodium acetate is hydrolysed to the extent of 0.008 per cent., the electrical conductivity of pure water at 25° is calculated to be 0.56×10^{-11} , and this conductivity is greatly diminished when electrolytes are present. A salt of a strong acid and a strong base is hydrolysed to the extent of 1.21×10^{-4} per cent. in decinormal solution, the absolute quantity of the hydrolysed part being almost independent of the concentration.

From the value for the electrolytic dissociation of pure water, it is possible to calculate the E.M.F. which must be used to develop from water, hydrogen and hydroxyl ions in a liquid already containing as many of these as are in normal solutions of strong acids or bases

The calculated value is 0·81 volt, whilst the experimental value of Le Blanc is 0·76 volt.

J. W.

Magnetic Rotation of Liquids and Salt Solutions. By O. SCHÖNROCK (*Zeit. physikal. Chem.*, **11**, 753—786).—The author has determined the magnetic rotation of the compounds used by Landolt and Jahn in their investigation of dielectric constants (*Berlin Sitz-Ber.*, 21st July, 1892). The measurements were made at temperatures ranging from 20° to 30° with the following results.

		Specific rotation.	Molecular rotation.
Water	H ₂ O	1·000	1·000
Pentane	C ₅ H ₁₂	1·45	5·81
Hexane	C ₆ H ₁₄	1·39	6·66
Octane	C ₈ H ₁₈	1·38	8·72
Decane	C ₁₀ H ₂₂	1·39	10·99
Amylene.....	C ₅ H ₁₀	1·59	6·18
Hexylene.....	C ₆ H ₁₂	1·60	7·45
Octylene.....	C ₈ H ₁₆	1·51	9·41
Decylene	C ₁₀ H ₂₀	1·45	11·25
Benzene	C ₆ H ₆	2·59	11·23
Toluene.....	C ₇ H ₈	2·35	12·03
Ethylbenzene	C ₈ H ₁₀	2·26	13·33
Orthoxylene	"	2·26	13·31
Metaxylene	"	2·16	12·73
Paraxylene	"	2·17	12·79
Propylbenzene.....	C ₉ H ₁₂	2·16	14·40
Isopropylbenzene	"	2·17	14·44
Mesitylene	"	1·94	12·92
Pseudocumene.....	"	2·06	13·77
Isobutylbenzene	C ₁₀ H ₁₄	2·09	15·53
Cymene.....	"	2·00	14·89
Methyl alcohol	CH ₃ O	0·913	1·62
Ethyl alcohol	C ₂ H ₅ O	1·07	2·73
Propyl alcohol	C ₃ H ₇ O	1·13	3·76
Isopropyl alcohol.....	"	1·19	3·97
Isobutyl alcohol.....	C ₄ H ₁₀ O	1·17	4·83
Amyl alcohol.....	C ₅ H ₁₂ O	1·20	5·89
Ethylenic chloride.....	C ₂ H ₄ Cl ₂	1·004	5·52
Ethylidenic chloride	"	0·976	5·36
Pyridine	C ₅ H ₅ N	2·01	8·82
Acetone.....	C ₃ H ₆ O	1·08	3·48
Diethyl ketone.....	C ₅ H ₁₀ O	1·14	5·43
Amyl ether.....	C ₁₀ H ₂₂ O	1·27	11·18

In order to investigate the influence of electrolytic dissociation on the rotation, the author measured the constants of various salts dissolved in water and other solvents. As most of the experiments

were made with mercury salts, which are very little dissociated even in aqueous solution, his results are inconclusive. Calcium chloride dissolved in water (12 per cent. solution) has a molecular rotation of 9.73, and dissolved in alcohol (5.67 per cent. solution) a molecular rotation of 8.62. Hydrogen chloride gives the same rotation whether dissolved in water or in amyl ether. The experiments, however, are not quite satisfactory, as a considerable portion of the amyl ether is converted into amyl chloride and amyl alcohol by the action of the hydrogen chloride.

The rotation of mixed salt solutions may be calculated from the rotations of the components, except in cases where complex salts, such as $2\text{KI}, \text{HgI}_2$, are formed. J. W.

Mercurial Thermometer for Temperatures up to 550°. By M. V. RECKLINGHAUSEN (*Ber.*, 26, 1514—1517).—The thermometer is made of Jena glass, No. 59III, and contains compressed carbonic anhydride. The author has made a number of determinations of the boiling points of sulphur, mercury, and of various organic compounds; the corrected numbers agree tolerably closely with the values obtained with the air thermometer. In the second part of his paper, the author records a number of experiments to decide the question of the existence of sulphides of phosphorus; mixtures of red phosphorus and sulphur in the proportions represented by $\text{P}_2 + \text{S}_6$, $\text{P}_2 + \text{S}_3$, $\text{P} + \text{S}_2$ respectively, were distilled; in general the boiling points showed a tendency to rise slowly. The values were for $\text{P}_2 + \text{S}_6$, 522.5—525°; for $\text{P}_2 + \text{S}_3$, 545—546.5°; for $\text{P} + \text{S}_2$, 516—519°. The subject is being further investigated. J. B. T.

Mercurial Thermometers to register up to 550°. By A. MAHLKE (*Ber.*, 26, 1815—1818).—The space above the mercury in these thermometers is filled with carbonic acid gas at a pressure of about 20 atmospheres. Their indications are accurate for temperatures up to 550°, but above this point the glass begins to soften, and the capacity of the bulb is increased by the internal pressure. The glass used in the construction is the variety of Jena glass known as 59III. In order to avoid the uncertainties of calculation in estimating the correction to be applied to these instruments for exposure of the stem, which may under certain circumstances amount to as much as 40°, the author recommends the use of a specially constructed thermometer with a long capillary mercury chamber which is placed close to the stem of the pressure thermometer. A. H.

Specific Heat of Water. By BARTOLI and STRACCIATI (*Ann. Chim. Phys.* [6], 29, 285—288).—The authors adopt as unity the specific heat of water at 15°. The total heat absorbed between 0° and t° by unit weight of water is given by the formula

$$Qt = 1.00663t - 0.000296981t^2 + 0.000001446217t^3 + 0.00000010638t^4 - 0.000000000564t^5.$$

The mean specific heat is obtained by dividing by t , and the true

specific heat by differentiating. The differences between the calculated and experimental values do not amount to 0·00005.

A. R. L.

Heats of Combustion of Gaseous Hydrocarbons. By BERTHELOT and MATIGNON (*Compt. rend.*, 116, 1333—1339).—The carefully purified hydrocarbons were burnt in the calorimetric bomb by means of compressed oxygen. The values obtained are as follows:—

	Hydrogen.	Carbonic oxide.	Methane.	Acetylene.
Heat of com- { const. vol....	68·15 Cal.	67·9	—	—
bustion ... { const. press...	68·99 "	68·2	213·5	315·7
Heat of formation.....	—	+26·1	+18·7	+58·1

	Ethylene.	Ethane.	Propane.	Allylene.	Propylene.	Trimethylene.
Heat of com- { const. vol...	340·05	370·9	526·7	472·4	497·9	505·6
bustion .. { const. press.	341·1	372·3	528·4	473·6	499·3	507·0
Heat of formation.....	-14·6	+23·3	+30·5	-52·6	-9·4	-17·1

The difference between the heats of combustion of two homologous and contiguous hydrocarbons is practically constant, the value being about 157 Cal. The corresponding difference between the heats of formation is about 5·5 Cal. It follows that in the methane series the heats of combustion at constant pressure are $213·5 + 157·5n$, in the ethylene series $341·2 + 157·5n$, and in the acetylene series $315·5 + 157·5n$, whilst the corresponding heats of formation are respectively $+18·7 + 5·5n$, $-14·6 + 5·5n$, and $-58·1 + 5·5n$.

The conversion of a member of the acetylene series into the corresponding olefine develops about 43·3 Cal., and the conversion of the olefine into the paraffin develops +39 Cal.

The heat of combustion of trimethylene does not agree with the view that it is a closed chain hydrocarbon. The heat of formation of trimethylene dichloride, +4·3 Cal., shows that the substitution of Cl_2 for H_2 produces a thermal disturbance similar to that observed in the methane series.

C. H. B.

Heat developed by the Combination of Bromine with Non-saturated Compounds of the Paraffin Series. By W. LOUGUININE and I. KABLUKOV (*Compt. rend.*, 116, 1197—1200).—The experiments were made in the laboratory vessel devised by Berthelot, the substance being dissolved in carbon tetrachloride in order to moderate the reaction. The compounds used were trimethylene, boiling at $38-38·5^\circ$; hexylene, boiling at $68-68·5^\circ$; diallyl, allyl alcohol, and allyl bromide, and the results obtained were as follows:—

$C_5H_{10} + Br_2 = C_5H_{10}Br_2 \dots\dots\dots$	develops	+ 27285 Cal.
$C_6H_{12} + Br_2 = C_6H_{12}Br_2 \dots\dots\dots$	„	+ 28843 „
$C_6H_{10} + 2Br_2 = C_6H_{10}Br_4 \dots\dots\dots$	„	+ 56114 „
$C_3H_6 + Br_2 = C_3H_6Br_2O \dots\dots\dots$	„	+ 27732 „
$C_2H_5Br + Br_2 = C_3H_5Br_3 \dots\dots\dots$	„	+ 26695 „

With diallyl, the compound $C_6H_{10}Br_2$ is formed simultaneously with the compound $C_6H_{10}Br_4$; with allyl alcohol, a notable quantity of hydrogen bromide is formed; with allyl bromide, combination takes place more slowly than in the other cases.

The authors conclude (1) that the heat of combination with bromine, in a homologous series, increases with the molecular weight of the hydrocarbon; (2) that when hydrogen has already been partially displaced by bromine, combination with this halogen takes place more slowly; and (3) when the hydrocarbon already contains a hydroxyl group, the reaction is no longer distinct, but combination is accompanied by substitution.

C. H. B.

Boiling Points and Melting Points of Sulphur Compounds.

By Miss A. G. EARP (*Phil. Mag.* [5], 35, 458—462).—From tables containing a large number of organic compounds, it is shown that the substitution of sulphur for oxygen in a compound always raises the boiling point, except in those cases in which the oxygen of a hydroxyl group is replaced by sulphur, and then the reverse effect is observed. Very few exceptions to this rule exist. The same general rule is stated to hold with regard to the melting points of oxygen and sulphur compounds, but exceptions are not rare, particularly in the case of the more complicated compounds. J. W.

Heat of Vaporisation of Hydrogen Chloride. By K. TSURUTA (*Phil. Mag.* [5], 35, 435—439).—The author has calculated the heat of vaporisation of hydrogen chloride, using the formula of Clausius, and the data of Ansdell, Biot and Arago, and Regnault. The values dp/dT were deduced from the following interpolation formula:—

$$p = 28.451 + 0.4914t + 0.012463t^2.$$

The heat of vaporisation is 61.02 Cal. at 4°. It then increases to nearly 66 Cal. at 14°, after which it falls steadily and slowly to 35.79 Cal. at 44.8°, the fall then becoming rapid, so that the heat of vaporisation vanishes entirely at 51.25°, the critical point, the value at 49.4° being still 23.5 Cal.

J. W.

Heat of Vaporisation of Organic Compounds. By H. JAHN (*Zeit. physikal. Chem.*, 11, 787—793).—The author has determined the heat of vaporisation of various organic compounds at 0° by means of Bunsen's ice calorimeter. The following table contains his results, L being the heat of vaporisation in gram-calories, and

$$c = L(k - 1)/d^2 \sqrt{k(k + 2)},$$

where k is the dielectric constant, and d the density.

	L at 0°.	C.
Methylic acetate	113·86	30·92
Ethylic formate	113·25	30·76
Ethylic acetate	102·14	30·20
Propylic formate	105·37	30·85
Ethylenic chloride	85·40	11·99
Ethylidenic chloride	76·77	12·34
Benzene (liquid)	107·63	25·83
Pentane	74·89	28·99
Hexane	89·16	31·99
Hexylene	92·46	34·21
Methyl alcohol	292·22	58·23
Ethyl alcohol	229·04	52·01

It will be observed that the value of c for analogous substances varies very little, and the author shows that, except in the case of the alcohols, it is for any one substance practically independent of the temperature.

J. W.

Critical Constants of some Organic Compounds. By M. ALTSCHUL (*Zeit. physikal. Chem.*, 11, 577—597).—The author has determined directly the critical temperature θ and pressure π of a number of organic compounds, and from the data so obtained has calculated the critical volume ϕ and the constants a and b of the Van der Waals' formula. The results are contained in the following table.

	θ .	π .	ϕ .	a .	b .
Pentane	187·1°	33·3	0·01958	0·03829	0·00653
Hexane	234·5	30·0	0·02449	0·05395	0·00816
Octane	296·4	25·2	0·03324	0·08351	0·01108
Decane	330·4	21·3	0·04264	0·11624	0·01421
Benzene	290·5	50·1	0·01596	0·03827	0·00532
Toluene	320·6	41·6	0·02051	0·05244	0·00684
Ethylbenzene	346·4	38·1	0·02354	0·06339	0·00785
Orthoxylene	358·3	36·9	0·02487	0·06852	0·00829
Paraxylene	344·4	35·0	0·02572	0·06945	0·00857
Metaxylene	345·6	35·8	0·02517	0·06795	0·00839
Propylbenzene	365·6	32·3	0·02912	0·08212	0·00971
Isopropylbenzene	362·7	32·2	0·02904	0·08147	0·00968
Mesitylene	367·7	33·2	0·02836	0·08012	0·00945
Pseudocumene	381·2	33·2	0·02901	0·08396	0·00967
Isobutylbenzene	377·1	31·1	0·03098	0·08947	0·01033
Paracymene	378·6	28·6	0·03400	0·09921	0·01133

In addition to the above, the critical temperatures only of the following were determined: Amylene, 208·0°; hexylene, 243·5° (?); octylene, 304·8°; diamylene, 341—342°; chlorobenzene, 362·2°.

H. C.

Vapour Pressures of Fatty Acids. By H. LANDOLT (*Zeit. physikal. Chem.*, 11, 633—644).—Discrepancies between the results

obtained by Schmidt for the vapour pressures of the fatty acids and those of the author have led the latter to repeat his determinations. He finds that a number of his former results, those applying to pressures at low temperatures, were undoubtedly too high, and has obtained new values which are intermediate between the previous ones and those of Schmidt. Tables of these values are given in the paper. The error is attributed to the method employed for making the determinations, measurement of the tension in barometer tubes over mercury, and is due to the extreme difficulty of completely removing all air from the tube. The author considers that the dynamical is to be preferred to the statical method of determining vapour pressures. H. C.

Internal Pressure in Solutions. By G. TAMMANN (*Zeit. physikal. Chem.*, **11**, 676—692).—From the change in the temperature of maximum density of water and different salt solutions by increased pressure, the author calculates the difference between the internal pressure (constant K of Laplace) of the pure water and that of the water in the solutions. The internal pressure is always higher in the case of the solution than in that of water, and the difference being known, it is possible to calculate changes in volume on compression of the solutions, or volume changes attending the dissolution of salts in water. H. C.

Cryohydric Quintuple Points. By W. MEYERHOFFER (*Monatsh.*, **14**, 177—185).—The author considers the conditions of equilibrium in a saturated solution of a double salt, AB , with one common ion, when in contact with the salt in the solid state. Such a system will have a cryohydric point, K_D , at which the saturated solution freezes. In addition to the solution of the double salt, two other saturated solutions are possible, those of $AB + A$ and $AB + B$. In the first $A > B$, and in the second $B > A$. These solutions also have cryohydric points, K_{D+A} and K_{D+B} . Each of these latter points is a quintuple point with five phases, in which five equilibria curves, corresponding each to four phases, meet. The author discusses the general character of the above curves, with the exception of the two belonging to the three solid phases and vapour, and the three solid phases and solution. H. C.

The Freezing Point of Dilute Solutions of Sodium Chloride. By H. C. JONES (*Ber.*, **26**, 1633—1639).—A controversial paper, in answer to Pickering.

Labile Conditions of Equilibrium in Salt Solutions. By A. BLÜMCKE (*Zeit. physikal. Chem.*, **11**, 645—656).—Theoretical considerations, on a thermodynamical basis, of certain special cases of labile equilibrium in solutions of hydrated salts. H. C.

Volume Changes in Aqueous Solutions. By M. ROGOFF (*Zeit. physikal. Chem.*, **11**, 657—660).—The volume changes which water undergoes when different salts are dissolved in it in equivalent pro-

portions with the formation of dilute solutions are found, on comparison, to be additive functions of the ions present in the salts. The changes are calculated from the numbers given by Ostwald for the specific volumes of certain salt solutions, 1 kilo. of each solution containing 1 gram equivalent of the base or acid present. Thus, in the case of potassium nitrate, the equivalent of which is 101.1, the water used is $2000 - 101.1 = 1898.9$ grams. After dissolution, the volume of the resulting solution is 1937.3 c.c., so that the change in the volume of the water is $1937.3 - 1898.9 = 38.4$ c.c. Other volume changes are calculated in like manner. The differences between the volume changes on dissolving two salts of two different bases, but one and the same acid, are independent of the nature of the acid, and if the same two bases be always taken, are constant. If two different acids with one and the same base be taken, a similar relationship holds, the differences between the volume changes being then independent of the nature of the base. A few exceptions to this rule, noticed in the case of arsenates, phosphates, and oxalates, are probably due to hydrolytic dissociation. In the case of several salts, the differences in the volume changes are very nearly equal to the differences in the molecular volumes of the dry salts, thus:

Difference in volume

change..... $\text{KCl} - \text{NaCl} = 10.4$. $\text{NaNO}_3 - \text{NaCl} = 11.2$.

Difference in mole-

cular volume $\text{KCl} - \text{NaCl} = 10.5$. $\text{NaNO}_3 - \text{NaCl} = 10.5$.

H. C.

Electrolytic Dissociation of Water. By G. BREDIG (*Zeit. physikal. Chem.*, 11, 829—831).—The author finds that the dissociation constant (K) of aniline at 25° is 11×10^{-7} , and from this result, together with the conclusions drawn by Arrhenius from the conductivity of aniline acetate solutions, calculates that the quantity of hydrogen or hydroxyl ions contained in a litre of pure water is 0.6×10^{-6} gram equivalents. This number agrees well with those recently found by Ostwald, Wijs, and Arrhenius.

J. W.

Hydrolysis in Aqueous Salt Solutions. By J. SHIELDS (*Phil. Mag.* [5], 35, 365—388).—When a salt, such as potassium cyanide, formed by the combination of a feeble acid with a strong base, is dissolved in water, it is partially hydrolysed into free acid and free base, the water playing the part of a feeble acid which displaces a portion of the hydrocyanic acid from its combination with the potash. The reaction is a balanced one, so that in different degrees of concentration the amount of hydrolysis varies. The quantity of free base in the solution cannot be estimated by methods depending directly on neutralisation, but it may be ascertained by determining the rate at which the solution saponifies an ethereal salt such as ethyl acetate. The constant of velocity of the saponification is, at any given temperature, proportional to the concentration of free alkali. Since, however, fresh quantities of alkali are supplied from the continued decomposition of the potassium cyanide, as the original quantity is used up in the process of saponification, it is necessary to allow for this by the law of mass action in the construction of the equations, which

assume somewhat different forms according as the salt is little or much hydrolysed.

The author has investigated a number of salts according to this method, and arrives at the following conclusions:—

1. The amount of hydrolysis in $\frac{1}{10}$ molecular normal solutions at 24–25° is as follows:—

Potassium cyanide.....	1·12 per cent.
Sodium carbonate	3·17 ,,
Potassium phenoxide.....	3·05 ,,
Borax (about).....	0·5 ,,
Sodium acetate	0·008 ,,

Trisodium phosphate is almost entirely hydrolysed into sodium hydroxide and disodium hydrogen phosphate, which is not itself appreciably decomposed.

2. When the salts are not hydrolysed to a great extent, the amount of free alkali in the solutions is nearly proportional to the square root of the concentration.

3. The presence of varying quantities of ethylic acetate does not materially disturb the equilibrium between the salt and water on the one side and the acid and base on the other.

J. W.

The Number of Saturated Solutions of a Double Salt. By W. MEYERHOFFER (*Monatsh.*, 14, 165—175; compare *Abstr.*, 1892, 1145).—The system $\text{CuCl}_2 + \text{NEt}_4\text{Cl} + \text{H}_2\text{O}$ has been examined, the system being capable of forming *two* double salts, $\text{CuCl}_2 \cdot 2\text{NEt}_4\text{Cl}$ (M), and $5\text{CuCl}_2 \cdot 2\text{NEt}_4\text{Cl}$ (P). Curves are given in which temperatures are plotted as abscissæ, and as ordinates the ratio, in molecules, of $\text{CuCl}_2 : \text{NEt}_4\text{Cl}$ in the saturated solution; this ratio is indicated by Cu/N . Up to 15·5°, three saturated solutions can exist at each temperature, containing respectively (1) $\text{M} + \text{NEt}_4\text{Cl}$, (2) M , (3) $\text{M} + \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. From 15·5° to 31·9° four saturated solutions are possible, containing (1) $\text{M} + \text{NEt}_4\text{Cl}$, (2) M , (3) $\text{M} + \text{P}$, and (4) $\text{P} + \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Above 31·9° five, containing (1) $\text{M} + \text{NEt}_4\text{Cl}$, (2) M , (3) $\text{M} + \text{P}$, (4) P , and (5) $\text{P} + \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Above a certain undetermined temperature, M will become incapable of existing by itself in solution, and we should then have four saturated solutions, (1) $\text{M} + \text{NEt}_4\text{Cl}$, (2) $\text{M} + \text{P}$, (3) P , and (4) $\text{P} + \text{CuCl}_2$. And above a yet higher temperature, also undetermined, the three following saturated solutions would be possible, (1) $\text{P} + \text{NEt}_4\text{Cl}$, (2) P , and (3) $\text{P} + \text{CuCl}_2$. Each of the five saturated solutions mentioned above is thus seen to be capable of existence only between fixed limits of temperature; the values of the ratio Cu/N , corresponding with these limits, are given below for the five solutions; they are at once evident on inspection of the curves. (1) $\text{M} + \text{NEt}_4\text{Cl}$, $\text{Cu}/\text{N} < \frac{1}{2}$; (2) M , $\text{Cu}/\text{N} = \frac{1}{2}$; (3) $\text{M} + \text{P}$, $\frac{5}{2} > \text{Cu}/\text{N} > \frac{1}{2}$; (4) P , $\text{Cu}/\text{N} = \frac{5}{2}$; (5) $\text{P} + \text{CuCl}_2$, $\text{Cu}/\text{N} > \frac{5}{2}$. Finally, the following rule is enunciated: “If two salts containing a common ion form at a given temperature n double salts, the latter and their components will at this temperature form at least $n + 1$, at most $2n + 1$, saturated solutions of different composition.”

C. F. B.

The Existence of Double Salts in Solution. By C. E. LINEBARGER (*Amer. Chem. J.*, 15, 337).—The author submits mixtures of two salts to the action of various organic liquids, one of the salts being insoluble in the liquid. If both salts are found to pass into solution in a simple molecular ratio, the conclusion is drawn that a double salt has been formed in the solution. When a mixture of mercuric chloride and sodium chloride is acted on by ethylic acetate, in which sodium chloride is insoluble, both salts dissolve, in the proportion of 2 mols. HgCl_2 : 1 mol. NaCl . This ratio is constant for temperatures from 0° to 50° , but at 140° the double salt decomposes, and sodium chloride is deposited. The existence of the double salt in solution is also proved by the fact that the addition of sodium chloride to a boiling solution of mercuric chloride in ethylic acetate does not raise the temperature of the boiling point. Analogous phenomena are observed with the same mixture of salts and acetone, with the chlorides of mercury and lithium and ethylic acetate, and with potassium or sodium chloride when mixed with cadmium bromide or iodide and treated with acetone or ethylic acetate.

A. H.

Conditions of Chemical Equilibrium. By S. BUGARSZKY (*Zeit. physikal. Chem.*, 11, 668—675).—Yellow mercuric oxide is dissolved, to some extent, by a salt solution, or, better still, by a solution of potassium bromide. In the latter case, the action takes place in accordance with the equation $2\text{KBr} + \text{HgO} + \text{H}_2\text{O} = 2\text{KOH} + \text{HgBr}_2$. This reaction is evidently of a reversible character, and will take place in the direct or reverse sense until conditions of equilibrium are established. The ordinary laws of mass action should hold in this as in other cases, and the author shows that, as a matter of fact, the establishment of equilibrium does take place after a certain period of time, and, further, that the active mass of the solid mercuric oxide may be regarded as constant. On the other hand, the product of the active masses on the right side of the equation divided by the product of the active masses on the left, which should be constant when equilibrium is established, is found to vary within wide limits, increasing rapidly with the dilution of the solutions. This exceptional behaviour may be explained, if it is assumed that it is not the whole mass of the dissolved salts which is active in promoting the above reaction, but only that portion which has undergone electrolytic dissociation, the reaction taking place in the sense of the equation $2\text{K}^+ + 2\text{Br}^- + \text{HgO} + \text{H}_2\text{O} \rightleftharpoons \text{HgBr}_2 + 2\text{K}^+ + 2\text{OH}^-$, and the mercuric bromide further undergoing partial dissociation, $\text{HgBr}_2 = \text{HgBr}^+ + \text{Br}^-$. In the author's experiments, the dissociation of the potassium salts in the solutions used may be regarded as complete, but that of the mercuric bromide increases with the dilution. The exceptional behaviour above recorded accords with this view.

H. C.

Affinity Coefficients of Aromatic Amidosulphonic acids. By F. P. EBERSBACH (*Zeit. physikal. Chem.*, 11, 608—632).—The

affinity coefficients of the following acids were determined, from the electrical conductivity of their solutions:—

Acid.	Affinity coeff. K.
$\text{HSO}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{NHMe}$ [= 1 : 4].....	0·0665.
$\text{HSO}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ [= 1 : 3]	0·0353.
$\text{HSO}_3 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{NO}_2$ [= 1 : 2 : 4].....	0·85.
$\text{HSO}_3 \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{NH}_2$ [= 1 : ? : ? : 3].....	0·16.
$\text{OH} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{HSO}_3$ [= 1 : 2 : 4].....	0·00941.
$\text{OH} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{HSO}_3$ [= 1 : 4 : 2].....	0·000831.
$\text{OH} \cdot \text{C}_6\text{H}_3\text{Cl}(\text{NH}_2) \cdot \text{HSO}_3$ [= 1 : 2 : 4 : 6]....	0·00822.
$\text{HSO}_3 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2$ [= 1 : 4 : 3]	0·0250.
$\text{HSO}_3 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2$ [= 1 : 3 : 2]	0·0753.
$\text{HSO}_3 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2$ [= 5 : 1 : 2].....	0·0850.
$\text{HSO}_3 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2$ [= 6 : 1 : 3].....	0·00408.
$\text{HSO}_3 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2$ [= 2 : 1 : 4]	0·0357.
$\text{HSO}_3 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ [= 1 : 4]	0·00234.
$\text{HSO}_3 \cdot \text{C}_6\text{H}_2\text{MeBr} \cdot \text{NH}_2$ [= 1 : 4 : ? : 3].....	0·14.
$\text{HSO}_3 \cdot \text{C}_6\text{HMeBr}_2 \cdot \text{NH}_2$ [= 1 : 4 : ? : ? : 3]...	3·0.
$\text{HSO}_3 \cdot \text{C}_6\text{H}_2\text{MeBr} \cdot \text{NH}_2$ [= 1 : 6 : ? : 3]	0·45.
$\text{HSO}_3 \cdot \text{C}_6\text{H}_2\text{Me}(\text{NH}_2)_2$ [= 1 : 5 : 2 : 4].....	0·0215.
$\text{HSO}_3 \cdot \text{C}_6\text{H}_2\text{Me}(\text{N}_2\text{H}_3) \cdot \text{NO}_2$ [= 1 : 5 : 2 : 4]...	0·013.

Several of the monosulphonic acids of the two naphthylamines were also examined, with the following results:—

α -Naphthylamine.	β -Naphthylamine.
Acid 1 : 2.... K = 2·20	
„ 1 : 4.... 0·20	
„ 1 : 5.... 0·0240	Acid 2 : 5.... K = 0·00940
„ 1 : 6.... 0·0195	„ 2 : 6 (?) 0·0166
„ 1 : 7.... 0·0227	„ 2 : 7.... 0·0102
„ 1 : 8.... 0·00102	„ 2 : 8.... 0·0122

H. C.

General Method of Chemical Synthesis. By R. PICTET (*Compt. rend.*, 116, 1057—1060).—The author has shown in a former paper (this vol., ii, 112) that all chemical action ceases at temperatures below -130° . It is, however, possible to produce chemical action in a mass cooled to this temperature by furnishing to it energy from the outside, in the form, for instance, of electric sparks. The quantities of energy supplied in this manner may be taken as equivalent to the endothermic phase of the reaction, and the heat lost by radiation to the surroundings as a measure of the exothermic phase. With the knowledge of these two quantities, the exact conditions necessary for effecting any particular chemical synthesis could be accurately ascertained and defined.

H. C.

The Atomic Weights of Stas. By J. D. VAN DER PLAATS (*Compt. rend.*, 116, 1362—1367).—A criticism of the discussions of Stas's results by Ostwald, and, more especially, by Hinrichs (this vol., ii, 163, 277).

C. H. B.

Conservation of Mass in Chemical Changes. By H. LANDOLT (*Ber.*, 26, 1820—1830; and more fully in *Zeit. physikal. Chem.*, 12, 1).—The author has carried out an extended series of experiments to ascertain (1) whether any change in weight occurs when two substances react chemically: Such a change might be due either to a change in the effect of gravity, or to an alteration of the mass, produced either by the interference of the ether, or by some other unknown cause. (2) Whether, if such a change does occur, its magnitude is sufficient to account for the deviation of the experimentally found atomic weights of the elements from the whole numbers required by Prout's hypothesis. The reactions are carried out in sealed glass vessels, of almost precisely equal weight and volume. These were of such a shape that the reagents could be gradually brought into contact after the vessels had been sealed. The difference of weight of the two vessels was then determined, the reaction allowed to proceed in one of them, the difference in weight again determined, and, finally, the reaction carried out in the second vessel and the difference again ascertained. The reactions chosen were, (1) the action of silver nitrate on ferrous sulphate in aqueous solution; (2) the action of hydriodic acid on iodic acid in aqueous solution; (3) the action of iodine on sodium sulphite in solution; (4) the action of caustic soda on chloral hydrate; and, finally, (5) the solution of solid chloral hydrate in water. Using from 100 to 200 grams of reacting substances, and with apparatus weighing from 670—990 grams, it was found that a greater accuracy than 0.1—0.2 milligram could not be depended upon; changes of this magnitude occurring in opposite directions in the course of a single series of experiments. Within these limits, no difference between the weights of the vessels before and after the reactions could be ascertained. In reaction (1), a loss of about 0.1 milligram per 100 grams of reacting substance was always observed, the effect of which, even if it were accepted as a definite change of weight, would only be to increase the atomic weight of silver by 0.0009. The results obtained, therefore, confirm those previously arrived at by Stas (*Nouv. Rech.* (1865), 152, 171, 189), and, more recently, by Kreichgauer (*Verh. physik. Gesellsch., Berlin*, 10, No. 2, 13), the latter of whom employed the same method as the author.

A. H.

New Laboratory Apparatus. By O. N. WITT (*Ber.*, 26, 1694—1698).—The author describes a laboratory press and a stirrer; the former differs from those in ordinary use, in the fact that the substance to be pressed is placed between two blocks of glazed porcelain, the faces of which are ribbed; the lower one is surrounded by a rim provided with a spout for the separation of the expressed liquid; the upper block is fitted with an iron cap, fastened with india-rubber, to receive the end of the screw. The blocks are unacted on by chemicals, can be readily cleaned, and will withstand considerable pressure.

The stirrer consists of a pear-shaped glass bulb, 20—25 mm. in diameter; the top end is fused to a glass rod, the other is open; the bulb is pierced with four holes, each the size of the open end, and arranged symmetrically around its greatest diameter; it is operated

by a turbine, at a speed of 5000 turns per minute, in the ordinary manner.

Liquids of very different specific gravity may be intimately mixed by means of this instrument, without any danger of loss, even when the vessel is almost full. J. B. T.

New Tap for Vacuum Desiccators. By O. ERNST (*Ber.*, 26, 1698—1699).—The tap is made from a tube in the form of a Latin cross, the side pieces serving as handles; one of the longer limbs is drawn out so as to admit of being fitted to a pump; the other limb is sealed at the end and blown to a conical bulb, which is ground to fit the desiccator. At one side is a small hole, and, by turning the tap, this can be made to coincide with a depression in the socket of the desiccator, and thus establish communication with the outside air. The author recommends the use of a mixture of lanoline with a little vaseline as a suitable lubricant. The advantages of this form of tap over those generally in use are not specially apparent. J. B. T.

Inorganic Chemistry.

Molecular Weight of Hydrogen Peroxide. By W. R. ORNDORFF and J. WHITE (*Amer. Chem. J.*, 15, 347).—See this vol., i, 579.

Hydrogen Bromide. By A. GASSMAN (*Chem. Centr.*, 1893, i, 771; from *Schweiz. Woch. Pharm.*, 31, 107—109).—Hydrogen bromide is readily prepared by adding bromine (385 grams) to a mixture of liquid paraffin (500 grams) and dry phosphorus in small pieces (50 grams); water (about 100 grams) is then gradually run in and the evolved gas purified by passage over moist phosphorus.

J. B. T.

The Densities of Certain Gases and the Composition of Water. By A. LEDUC (*Compt. rend.*, 116, 1248—1250).—The author discusses the agreement or otherwise between the results obtained by Regnault, Jolly, Rayleigh, and himself for the densities of nitrogen, oxygen, and hydrogen. His value for nitrogen, 0.97203, differs from that obtained by Rayleigh, 0.97209, by an amount smaller than the experimental error. He contends that Rayleigh's results simply show that the ratio of the densities of hydrogen and oxygen lies between 15.912 and 15.856, and that there is no proof that the ratio is 15.882. Further, in the case of hydrogen, the lower numbers are the more probable, whilst the reverse would seem to be true for oxygen. Critical examination of the results obtained by Rayleigh, Morley, Scott, and the author himself, leads to the conclusion that the volume ratio of hydrogen and oxygen in water is greater than 2.0032, and that the atomic weight of oxygen is most probably 15.83 when $H = 1$.

C. H. B.

Formation of Ozone at High Temperatures. By O. BRUNCK (*Ber.*, 26, 1790—1794).—It has long been known that oxygen made from a mixture of potassium chlorate and manganese dioxide has an intense odour, resembling that of chlorine, and numerous statements have been made as to the amount of chlorine present in the gas. If chlorine is really produced in the reaction, free alkali must also be formed, and should be found as such in the residue or in the form of potassium manganate. The aqueous extract of the residue is, however, always completely neutral and colourless, and the gas evolved still has the power of liberating iodine from potassium iodide after washing with potash; it appeared therefore probable to the author that this property is really due to the presence of ozone. Experiments with ozonised oxygen showed that the ozone is not completely converted into oxygen at the temperature of the decomposition of potassium chlorate, provided it is only exposed to that temperature for a short time. The gas evolved from the potassium chlorate and manganese dioxide oxidises alcohol to aldehyde, but loses its odour and oxidising properties when passed over a short layer of manganese dioxide, and the source of these properties must, therefore, be ozone. The ozone thus formed appears, however, to differ to some extent from ordinary ozone; thus, its odour is almost exactly the same as that of chlorine, it is more stable towards heat, does not affect the surface of mercury, and attacks organic substances, such as caoutchouc, much less readily than the ozone obtained in the usual manner.

Absolutely pure potassium chlorate yields no ozone, but the presence of a trace of silica, or other indifferent compound, brings about the formation of ozone. A mixture of equal parts of manganese dioxide and potassium chlorate yields a gas containing 0.3 per cent. of ozone, the amount of the latter increasing with an increase in the proportion of dioxide, until with 25 times as much dioxide as chlorate the quantity of ozone amounts to 1.55 per cent.

In order to ascertain, if possible, the part played by the manganese dioxide in the reaction, the author has examined the behaviour of this and numerous other oxides at high temperatures. The investigation, although not yet complete, shows that the oxides examined may be divided into three classes: first, those which are quite indifferent, such as the oxides of iron, copper, and zinc; second, those which, on heating to their temperature of decomposition in an atmosphere free from oxygen, yield ozone, the amount of which is increased by heating them in a stream of oxygen, but disappears altogether when the oxide is heated with potassium chlorate; this group contains silver oxide, mercuric oxide, lead dioxide, and probably barium peroxide. The oxides of the third group give no ozone in absence of oxygen, but yield considerable quantities of it when heated to their temperature of decomposition in the latter gas, and also evolve ozone when heated with potassium chlorate at temperatures considerably below the point of decomposition of the salt; to this group belong manganese dioxide, cobalt oxide, and probably nickel sesquioxide. In all cases the presence of alkalis completely prevents the formation of ozone, and if sodium carbonate be added to the mixture the residue contains sodium peroxide.

H. G. C.

Note.—The author makes no reference to the work of MacLeod (Trans., 1889, 184).
H. G. C.

Plastic Sulphur from Sulphur Vapour. By J. GAL (*Compt. rend.*, 116, 1373—1375).—When sulphur vapour is condensed on the cold surface of a liquid (compare Abstr., 1892, 1150), the elasticity of the product varies with the conditions. Water, nitric and hydrochloric acids, and solutions of sodium and potassium hydroxides and sulphurous acid at 0° give practically the same result, the product containing 45 per cent. of insoluble sulphur. With sulphuric acid, the proportion of insoluble sulphur is as high as 75 per cent., whilst with ammonia it is as low as 15 per cent. In the last case the product is not soft, but forms brittle plates. There is, however, no relation between the elasticity of the product and the proportion of insoluble sulphur that it contains; the sulphur condensed on the surface of a block of ice is very elastic, but only 20 per cent. of it is insoluble.

Experiments were made on the influence of the temperature of the sulphur vapour and the temperature of the liquid on which it condenses. For one and the same condensing liquid, the proportion of insoluble sulphur is higher the higher the temperature of the sulphur vapour. With sulphuric acid and sulphur vapour at 300°, variation in the temperature of the acid between 0° and 160° has no influence on the insolubility of the product. With sulphur vapour at 440° and sulphuric acid, or with sulphur vapour at 300° or 440° and water, or liquid sulphur at 440° and water, the proportion of insoluble sulphur in the product is higher the lower the temperature of the condensing liquid.

If the flame of hydrogen sulphide or carbon bisulphide is allowed to impinge on the surface of a cold liquid, the hydrogen or carbon burns before the sulphur, and the latter is condensed in a plastic condition.

C. H. B.

Basic Metallic Sulphites. By K. SEUBERT and M. ELTEN (*Zeit. anorg. Chem.*, 4, 44—95).—The reaction which occurs when equivalent aqueous solutions of sodium sulphite and of a metallic salt are mixed in equal proportions has been studied, the former solution being poured into the latter. The solutions usually contained 1 mol. or $\frac{1}{10}$ mol. per litre, and the reaction took place at the ordinary temperature, but, especially when the normal sulphite was obtained under these conditions; efforts were made to obtain a more basic one by carrying out the precipitation at 100° instead of at 15°, or by boiling the precipitate of normal sulphite with water. In some cases, from iron onwards, solutions containing more than 1 mol. per litre were also used, and heated together at 100° in a sealed tube. The sulphite was usually obtained as a precipitate, rarely crystallised; it was washed with water, sometimes, if readily soluble in water, with alcohol, as also when it oxidised readily, in which case the washing was carried out in an atmosphere of hydrogen, and the ratio only of metal to sulphurous acid determined in the moist precipitate; combined water could not, of course, be then determined. The metal in the precipitate was estimated in the usual way; the sulphurous acid was determined by adding the precipitate to excess of standard iodine solution and titrating the excess of the latter with thiosulphate; or by

heating it with hydrochloric acid and a weighed quantity of potassium chlorate, and estimating the amount of chlorine evolved by means of the iodine which it liberated from potassium iodide, the amount by which this fell short of that theoretically obtainable from the chlorate being the amount used up in oxidising the sulphite to sulphate; or, finally, by oxidising the precipitate with a hydrochloric acid solution of bromine, and weighing the sulphate formed as barium sulphate. The combined water was not estimated directly. Below are given the formulæ of the compounds obtained; they are, in some cases, only approximately true. Carbonates were sometimes prepared, in order to compare their composition with that of the sulphites obtained under similar conditions; their formulæ are given in brackets. Except where indicated, the compounds were not obtained crystallised.

Copper.— $4\text{CuSO}_3, 3\text{Cu}(\text{OH})_2 + 5\text{H}_2\text{O}$; when boiled with water this yields Chevreul's salt, $\text{Cu}_2\text{SO}_3, \text{CuSO}_3 + 2\text{H}_2\text{O}$ (cryst.). *Silver*.— Ag_2SO_3 .

Beryllium.— $2\text{BeSO}_3, 9\text{Be}(\text{OH})_2 + 6\text{H}_2\text{O}$ [$\text{BeCO}_3, 5\text{Be}(\text{OH})_2 + 3\text{H}_2\text{O}$]. *Magnesium*.— $\text{MgSO}_3 + 6\text{H}_2\text{O}$ (cryst.); $11\text{MgSO}_3, 2\text{Mg}(\text{OH})_2 + 22\text{H}_2\text{O}$ (?). *Calcium*.— $\text{CaSO}_3 + \frac{1}{2}\text{H}_2\text{O}$ (cryst.). *Strontium*.— $\text{SrSO}_3 + \frac{1}{2}\text{H}_2\text{O}$ (cryst.). *Barium*.— BaSO_3 (cryst. ?).

Zinc.— $8\text{ZnSO}_3, 7\text{Zn}(\text{OH})_2 + 7\text{H}_2\text{O}$; $5\text{ZnSO}_3, 8\text{Zn}(\text{OH})_2$ (compare Abstr., 1891, 1157). *Cadmium*.— $\text{CdSO}_3 + 2\text{H}_2\text{O}$ (cryst.). *Mercury*.— $\text{HgSO}_3, \text{Na}_2\text{SO}_3 (+ \text{H}_2\text{O} ?)$.

Aluminium.— $\text{Al}_2(\text{SO}_3)_3, 3\text{Al}_2(\text{OH})_6 + 9\text{H}_2\text{O}$ [$\text{Al}_2(\text{CO}_3)_3, 5\text{Al}_2(\text{OH})_6 + 9\text{H}_2\text{O}$; also $2\text{Al}_2(\text{CO}_3)_2, 3\text{Al}_2(\text{OH})_6 + 28\text{H}_2\text{O}$].

Thallium.— Tl_2SO_3 .

Tin.— SnSO_3 (or $16\text{SnSO}_3, \text{Sn}(\text{OH})_2 ?$). *Lead*.— PbSO_3 .

Bismuth.— $(\text{BiO})_2\text{SO}_3, 3\text{Bi}(\text{OH})\text{SO}_3 + \text{H}_2\text{O}$; also in ratio 3 : 7 : 10, 2 : 3 : 2, 4 : 1 : 5, and 9 : 1 : 2; [$(\text{BiO})_2\text{CO}_3 + \frac{1}{2}\text{H}_2\text{O}$].

Chromium.— $\text{Cr}_2(\text{SO}_3)_3, 2\text{Cr}_2(\text{OH})_6 + 6\text{H}_2\text{O}$; $8\text{Cr}_2(\text{SO}_3)_3, 7\text{Cr}_2(\text{OH})_6 + 54\text{H}_2\text{O}$. *Uranium*.— $(\text{UO}_2)_2\text{SO}_3 + 4\text{H}_2\text{O}$ (cryst.);

$5(\text{UO}_2)_2\text{SO}_3, 3\text{UO}_2(\text{OH})_2 + 10\text{H}_2\text{O}$ [$3(\text{UO}_2)\text{CO}_3, 5\text{UO}_2(\text{OH})_2 + 6\text{H}_2\text{O}$].

Manganese.— $\text{MnSO}_3 + 3\text{H}_2\text{O}$; $5\text{MnSO}_3, 2\text{Mn}(\text{OH})_2 + 8\text{H}_2\text{O}$ and $+ 11\text{H}_2\text{O}$.

Iron.— $\text{FeSO}_3 + 5\text{H}_2\text{O}$ (cryst.) and $+ 2\text{H}_2\text{O}$; $2\text{Fe}_2(\text{SO}_3)_3, 7\text{Fe}_2(\text{OH})_6$; $\text{Fe}_2(\text{SO}_3)_3, 3\text{Fe}_2(\text{OH})_3$ [$\text{Fe}_2(\text{CO}_3)_3, 29\text{Fe}_2(\text{OH})_6$]. *Cobalt*.—

$5\text{CoSO}_3, \text{Co}(\text{OH})_2 + 10\text{H}_2\text{O}$;

$10\text{CoSO}_3, \text{Co}(\text{OH})_2 + 15\text{H}_2\text{O}$. *Nickel*.— $2\text{NiSO}_3, \text{Ni}(\text{OH})_2 + 6\text{H}_2\text{O}$.

It will thus be seen that silver, calcium, strontium, barium, cadmium, and mercury (as a double salt), thallium, lead, and iron (ferrous) form normal sulphites under all circumstances; magnesium, zinc, tin (stannous), uranium (uranyl), and manganese form normal sulphites under some conditions, more or less basic ones under others; and copper, beryllium, aluminium, bismuth, chromium, iron (ferric), cobalt, and nickel always form basic sulphites. There is a general similarity to the carbonates, but the latter have even a greater tendency to form basic salts; for instance, basic carbonates of lead, mercury, and, perhaps, silver, are obtained by double decomposition, although the sulphites formed under similar circumstances are normal.

C. F. B.

Absorption of Hydrogen Selenide by Liquid Selenium at a High Temperature. By H. PÉLABON (*Compt. rend.*, 116, 1292—1295).

—When selenium is heated in a sealed tube containing hydrogen, hydrogen selenide is formed, and, as the tube cools, the melted selenium gives off some gas which it had absorbed at the higher temperature. Direct analysis shows that this gas contains a considerable proportion of hydrogen selenide. If some selenium, after heating in the manner described, is powdered under water, and the latter is rapidly filtered and then exposed to the air, it becomes red, owing to the separation of selenium by the action of the oxygen of the air on the dissolved hydrogen selenide.

C. H. B.

Double Halogen Compounds of Tellurium with Potassium, Rubidium, and Cæsium. By H. L. WHEELER (*Zeit. anorg. Chem.*, 3, 428—440).

—A series of salts of the general formula $2RHI, TeHI_4$, in which $R = K, Rb, \text{ or } Cs$, and $HI = Cl, Br, \text{ or } I$. The method of preparation consists in all cases in adding the aqueous alkali haloid to a solution of telluric haloid in weak haloid acid, an excess of the latter being present to prevent the decomposition of the salt by the water, and consequent precipitation of tellurous acid. The relative proportion of the haloïds is in most cases immaterial. The salts are all soluble in weak solutions of the corresponding haloid acid, but are precipitated from these solutions by the addition of stronger acid. With the exception of the potassium double bromide and iodide, all are anhydrous, and crystallise in regular octahedra. The cæsium iodide, however, is amorphous. The two hydrated salts, with $2H_2O$, crystallise, the bromide in orthorhombic, the iodide in monoclinic, form. The chlorides are yellow, the bromides orange to scarlet, and the iodides black.

Potassium tellurichloride, except in the presence of a large excess of telluric chloride, tends to carry down potassium chloride with it, and this circumstance has led previous workers to erroneous formulæ. It is deliquescent. The *rubidium* and *cæsium* salts are both stable in air. *Potassium telluribromide* crystallises in anhydrous octahedra when its solution is evaporated quickly, but in hydrated orthorhombic crystals with $2H_2O$ when the evaporation is spontaneous. The hydrated salt is liable to enclose mother liquor, causing the analytical results for water of crystallisation to appear too high. The *rubidium* and *cæsium* salts are both stable in air. *Potassium telluriiodide* forms black, hydrated, monoclinic prisms with $2H_2O$; $a:b:c = 0.7047:1:0.5688$; $\beta = 59^\circ 7' 16''$. Unlike the bromide and chloride, it does not form an anhydrous salt. The *rubidium* salt crystallises in microscopic octahedra, but the *cæsium* salt is amorphous, and somewhat unstable in air.

JN. W.

Crystalline Nature of Red Phosphorus. By J. W. RETGERS (*Zeit. anorg. Chem.*, 3, 399—403).

—Seeing that red phosphorus occasionally assumes a sandy form, it seems not improbable that it may be crystalline. This supposition is confirmed by examination under the microscope and in polarised light. The smallest and thinnest particles are distinctly transparent, although, owing to their

high refractive power, most of the light, with the exception of a central red glimmer, is internally reflected. When, however, the phosphorus is moistened with a highly refractive liquid, such as methylenic iodide, to diminish the internal reflection, the particles transmit a clear, ruby-coloured light. In polarised light, these show extinction in two mutually perpendicular planes, and it is thus tolerably certain that they are crystalline, for the refractive power is too great to be accounted for by the assumption of internal stress in an amorphous medium. There is, however, no appreciable pleochroism. The crystalline system has not been determined, for although a few short prisms were observed, there were no rectilinear edges from which the system could be deduced.

Since the black or "metallic" variety of phosphorus, prepared by Hittorf (*Ann. Phys. Chem.*, **126**, 217) by heating red phosphorus to 500° and then dissolving it in, and recrystallising it from, melted lead, transmits red light, and has a sp. gr. (2·34) appreciably the same as that of the red variety (2·19), but distinctly different from that of the yellow variety (1·83), and as, moreover, the first two substances unite also in their low electrical resistance and their infusibility in offering a contrast to the last, it is not improbable that the black variety is merely a better crystallised form of the red variety, bearing somewhat the same relation to it that precipitated calcium carbonate bears to calc-spar. The black colour may be due to impurities, such as arsenic phosphide or metallic lead. JN. W.

Note.—The author entirely ignores Pedler's investigations (*Trans.*, 1890, 599).—[EDITORS.]

Red Phosphorus. By W. MUTHMANN (*Zeit. anorg. Chem.*, **4**, 303—304).—Retgers (preceding abstract) has denied the amorphous character of red phosphorus. The author points out that red phosphorus is dimorphous, and that the commercial product is frequently a mixture of the crystalline and the amorphous forms. When vitreous phosphorus is heated in an atmosphere of carbonic anhydride at 230° for 24 hours, the product is for the most part amorphous, but crystalline in places. If the experiment is performed in a glass tube, a sublimate of amorphous red phosphorus is formed, and is readily distinguished from the crystalline portion, which does not sublime, by its bright orange-red colour, the crystals having a violet tint; the greater ease with which it may be pulverised is also characteristic. In its optical properties this sublimate maintains its amorphous character. Inasmuch as the sublimed portion should, in the author's opinion, be accounted purer than the rest, it appears that the presence of impurities, for instance arsenic, favours the formation of crystals (compare Troost and Hautefeuille, this Journal, 1873, 599; 1874, 769).

A. G. B.

Phosphorus Sulphides. By M. v. RECKLINGHAUSEN (*Ber.*, **26**, 1514—1517).—See this vol., ii, 443.

Normal Thiophosphates. By E. GLATZEL (*Zeit. anorg. Chem.*, **4**, 186—226; compare *Abstr.*, 1892, 413).—The normal thiophos-

phates are prepared by heating either the chlorides or sulphides of the metals with phosphorus pentasulphide; in the former case thiophosphoryl chloride is also produced. The process is conducted in all cases in a manner similar to that prescribed for the preparation of antimony thiophosphate (Abstr., 1892, 413).

Attempts to prepare sodium, ammonium, barium, strontium, and calcium thiophosphates proved futile; the potassium salt could not be purified from phosphorus pentasulphide.

Zinc, nickel, lead, stannous, bismuth, cuprous, and silver thiophosphates were prepared from the corresponding chlorides and phosphorus pentasulphide; *manganese, thallous, mercuric, and arsenic thiophosphates* were better obtained from the corresponding sulphides and phosphorus pentasulphide. Attempts to prepare the ferric, stannic, cupric, and mercurous salts by the action of phosphorus pentasulphide on anhydrous ferric chloride, stannic sulphide, cupric chloride or cupric sulphide, and mercurous chloride, respectively, resulted in the production of iron pyrites (Abstr., 1890, 338) and stannous, cuprous, and mercuric thiophosphates respectively.

The formation of a thiophosphate from phosphorus pentasulphide and a metallic chloride or sulphide appears to take place more readily the more negative the metal.

Manganese, zinc, ferrous, nickel, cadmium, and cuprous thiophosphates are crystalline powders; lead, thallium, stannous, bismuth, silver, mercuric, antimony, and arsenic thiophosphates are fusible substances which crystallise as they solidify. The manganese salt is green; the zinc and cadmium salts are white; the ferrous, nickel, lead, stannous, and bismuth salts are more or less black; the thallous, cuprous, silver, antimony, arsenic, and mercuric salts are red, the last-mentioned being very sensitive to light. The powder of the lead salt is yellowish-green, that of the stannous salt is yellow, and that of the bismuth salt reddish-brown.

The thiophosphates impart a livid appearance to the colourless bunsen flame, and evolve sulphurous anhydride when heated in air. When heated in absence of air, mercuric and arsenic thiophosphates can be distilled unchanged; lead, thallous, stannous, bismuth, silver, and antimony thiophosphates melt easily without apparent decomposition, whilst zinc, ferrous, nickel, cuprous, and cadmium thiophosphates decompose into the corresponding metallic sulphides and phosphorus pentasulphide. Nickel sulphide is left by the decomposition of the thiophosphate in the form of yellow crystals of a metallic appearance.

Solvents have no effect on the thiophosphates; dilute acids partially decompose them with evolution of hydrogen sulphide; nitric acid oxidises and dissolves them; alkalis are for the most part without action on them. The impure potassium thiophosphate evolves hydrogen sulphide when in contact with water.

A. G. B.

Compounds of Arsenic Trioxide with Sulphuric Anhydride.

By A. STAVENHAGEN (*Zeit. angew. Chem.*, 1893, 283—284).—During the repair of a pyrites furnace, Redemeister noticed several large, transparent crystals which rapidly vanished in contact with the air, yielding sulphuric acid and a residue of arsenic trioxide. It was

therefore only with some difficulty that a few undecomposed pieces could be selected and subjected to analysis, which showed the compound to have the formula $\text{As}_2\text{O}_3(\text{SO}_3)_3$. Reich has described a similar product, which, however, had the formula $\text{As}_2\text{O}_3\text{SO}_3$. Weber has described a compound prepared by heating a mixture of arsenic trioxide with sulphuric anhydride at 100° which has the same composition as the crystals analysed by the author.

When arsenic trioxide is warmed with fuming sulphuric acid, it readily dissolves, and on cooling fine needles are deposited which, according to Schulz-Sellac, have the formula $\text{As}_2\text{O}_3(\text{SO}_3)_3 + \text{SO}_3$. (The author, however, failed to confirm this formula.) When a solution of the oxide in common sulphuric acid was evaporated, there was but little volatilisation of arsenic, and the syrupy liquid, after cooling, formed a vitreous mass of the same composition.

When evaporating a solution of arsenic trioxide in sulphuric acid until no more sulphuric fumes were given off, the author also obtained a vitreous mass, but of the composition $\text{As}_2\text{O}_2\text{SO}_3$. It is therefore beyond doubt that arsenic trioxide, like the corresponding antimony compound, behaves towards the stronger acids as a base.

L. DE K.

Manufacture of Borax. By H. N. WARREN (*Chem. News*, **67**, 244—245).—An intimate mixture of well-ground common salt and boric acid is introduced into an acid-proof, tubulated clay retort, and heated to slightly above a low red heat, when sufficient superheated steam is admitted through the tubulure to condense the hydrochloric acid which is evolved, the acid being collected in a cooled receptacle attached to the retort neck. Ultimately anhydrous borax only is left in the retort, and this is thrown, while still hot, into cold water and crystallised.

D. A. L.

New Alkali Borates. By A. REISCHLE (*Zeit. anorg. Chem.*, **4**, 166—177; compare Le Chatelier, *Abstr.*, 1892, 404).—*Lithium orthoborate*, $\text{Li}_2\text{H}_4\text{B}_2\text{O}_6 + 14\text{H}_2\text{O}$, was prepared by mixing aqueous solutions of boric acid, and of lithium oxide made by igniting the nitrate in hydrogen, and evaporating to crystallisation in a vacuum. It forms thin, hexagonal tables, which are described in detail in the paper, together with the method of analysis. The water of crystallisation is lost at 110° , the remainder at 160° . *Lithium metaborate*, LiBO_2 , is obtained on precipitating an alcoholic solution of lithium ethoxide with an alcoholic solution of boric acid, as a white, crystalline precipitate which retains alcohol when dried in a vacuum.

Rubidium borate, $\text{Rb}_2\text{B}_4\text{O}_7 + 6\text{H}_2\text{O}$, was prepared by Reisig (*Annalen*, **127**, 33); the author has confirmed his statements, and has also prepared the anhydrous *tetraborate*, $\text{Rb}_2\text{B}_4\text{O}_7$, by precipitating an alcoholic solution of rubidium oxide with a similar solution of boric acid.

Cæsium borate, $\text{Cs}_2\text{B}_6\text{O}_{10}$, is prepared in the same way as rubidium tetraborate; it separates slowly from the alcoholic solution as a white, crystalline precipitate.

A. G. B.

Volatilisation of Silica. By P. SCHUTZENBERGER (*Compt. rend.*, **116**, 1230).—The volatilisation of silica observed by Moissan

explains certain facts previously observed by the author, namely, that when pure silica is heated at a high temperature in a gas-carbon crucible brasqued with lamp black, there is a distinct loss of weight; and that when platinum is strongly heated it increases in weight, becomes fusible, and contains silicon, even though it is separated from siliceous matter by a layer of carbon. Silicon, on the contrary, seems to be non-volatile. C. H. B.

Combustion of Carbon in Air. By R. ERNST (*J. pr. Chem.* [2], 48, 31—45).—The course of the formation of carbonic oxide in a producer was studied by heating coke in a porcelain tube through which a current of air was passing, and analysing the products of combustion. An arrangement is figured and described in the paper, by means of which the gases can be collected, without undue contact with water, in Hempel's burettes, and subsequently analysed over mercury. The methods of analysis are detailed. The length of the layer of coke, the temperature, and the rate of passage of the air were varied in the different sets of experiments. The temperature was measured by a Le Chatelier platinum | platinum-rhodium pyrometer.

Tabulation of the conditions and results shows, in the author's opinion, that the composition of the products of combustion depends almost exclusively on the temperature. The formation of carbonic anhydride begins at about 400° , and at this temperature there is already a small quantity of carbonic oxide produced. The maximum production of carbonic anhydride occurs at about 700° , and amounts to some 20 per cent. of the products (including the nitrogen of the air used); up to this temperature the formation of carbonic oxide is but small, hardly exceeding 3 per cent.; the oxygen, however, is entirely used. At higher temperatures, the carbonic anhydride rapidly disappears, giving place to carbonic oxide, until at 995° this gas amounts to 34 per cent., the remainder being atmospheric nitrogen. It must be noted, however, that the rate of passage of the air was much reduced in those experiments in which the highest temperatures were maintained; no reason is assigned for this. There was no further change in the composition of the products up to the highest temperature (1092°) at which the author experimented. The production of carbonic oxide could not be induced at a lower temperature by altering the other experimental conditions.

It is concluded that carbonic oxide is the only oxidation product of carbon at 1000° , and that producer gas should be prepared at this temperature. By substituting carbonic anhydride for air, it was proved that this gas is never entirely reduced to carbonic oxide by the hot fuel, so that, where the production of carbonic oxide is preceded by that of carbonic anhydride, some of this gas must appear among the products of combustion; it may be concluded, therefore, that the carbon burns directly to carbonic oxide.

In the rational furnace, where a high temperature is required, the air supplied directly to the fuel must be only sufficient to burn it to carbonic oxide, which must subsequently be burnt by admission of fresh air. The temperature must be maintained at 995° and upwards.

The observation that coke burns without flame at moderate temperatures, but with flame at higher temperatures, is now explicable.

A. G. B.

Action of Oxygen on Sodammonium and Potassammonium.

By A. JOANNIS (*Compt. rend.*, 116, 1370—1373).—When pure and dry oxygen is passed into a solution of sodammonium or potassammonium in liquid ammonia at about -50° , the oxygen is rapidly absorbed, and the colour of the solution first becomes blue-black, and then the colour gradually disappears. With care, the quantity of oxygen required to decolorise the solution can be ascertained. The ammonium derivative is converted into a gelatinous precipitate resembling aluminium hydroxide.

The product from sodammonium is a white powder with a rosy tint, and it dissolves in water with great development of heat, but without any evolution of gas. It has the composition $\text{NH}_3\text{Na}_2\text{O}$ or $\text{NH}_2\text{Na}_2\text{OH}$. The compound $\text{NH}_2\text{Na}_2\text{Cl}$ has previously been obtained by the action of sodium chloride on sodammonium.

By prolonged action of oxygen on the ammonia solution, a rose-coloured product, Na_2O_3 , is obtained; this, when treated with water, evolves oxygen, and yields the hydrated dioxide described by Vernon Harcourt. Both the compounds $\text{NH}_3\text{Na}_2\text{O}$ and Na_2O_3 form at the beginning if the current of oxygen is too rapid.

In the case of potassammonium, if the current of oxygen is slow, the product at the moment of decolorisation is K_2O_3 , a rose-coloured, gelatinous precipitate. If the passage of the oxygen is continued, the colour of the precipitate changes to brick-red, and at the moment when this colour is deepest the product has the composition K_2O_3 . Further action of the oxygen changes the colour to chrome-yellow, and the ultimate product is K_2O_4 .

The dioxide dissolves in water, and yields a somewhat stable solution with powerful oxidising properties. The tetroxide also dissolves in water, with abundant evolution of oxygen. With a very small quantity of water, the dioxide reacts violently and even explosively, and seems to split up into the tetroxide and metallic potassium.

C. H. B.

Water as a Catalyst. By R. E. HUGHES (*Phil. Mag.* [5], 35, 531—534).—Silver chloride, prepared in the dark, dried perfectly in an air-bath, and then placed on a watch-glass in a desiccator partially exhausted, was found not to be perceptibly darkened in sunlight, even after an exposure of some hours; whereas a rapid darkening took place when moisture was introduced. Paper, when moistened with potassium iodide solution and exposed to the light, assumes a brownish-violet tint. As the staining varies very greatly with different kinds of paper, being greatest with highly-glazed note-paper, the author attributes it to the presence in the paper of chlorine.

When dry hydrogen chloride was passed over dry silver nitrate, either at the ordinary temperature or at 100° , it was found that only about 1 per cent. of the theoretical change had taken place after two hours. Hydrogen chloride acts on dry manganese dioxide, whether moisture is excluded or not.

Dried hydrogen chloride only produces a slight turbidity with a

solution of silver nitrate in hot, dry benzene or ether. With absolute alcohol as solvent, the amount of precipitate obtained is somewhat greater. Mercuric chloride in absolute alcohol forms a greenish-yellow precipitate with dried hydrogen sulphide only after a long time.

When dry ammonia and dry hydrogen chloride are mixed, they do not combine (compare Baker, *Proc.*, 1893, 129). J. W.

Atomic Weight of Barium. By T. W. RICHARDS (*Zeit. anal. Chem.*, 3, 441—471).—Barium bromide was eventually found to be the most suitable barium compound for the estimation of the atomic weight. The method finally adopted consisted in determining the equivalents of barium bromide in terms both of free silver and of silver bromide. Full details are given of the purification of the various substances used.

In the actual analysis, the barium bromide was gradually heated to redness, and the anhydrous salt weighed and dissolved in water, the slight amount of hydroxide and carbonate formed during the ignition being neutralised and estimated by standard hydrobromic acid. A solution of a known weight of silver in nitric acid, prepared in accordance with Stas's directions, was then added in the usual way, and the excess of silver or bromine determined by titration, the end point being repeatedly estimated both by direct and backward titration. In some cases, the bromide was added to the silver, a method of procedure which tended to increase the difference between the two end points without, however, altering their mean value. To furnish the data for the second series of determinations, the silver bromide was washed by decantation, collected in a Gooch crucible, dried (in some cases fused), and weighed. In certain cases, the barium bromide was used in the hydrated state, a concurrent determination of moisture being made on an approximately equal quantity.

The mean result of some 19 analyses gives the ratio $\text{Ag} : \text{BaBr}_2 = 1 : 1.37749$ and the ratio $\text{AgBr} : \text{BaBr}_2 = 1.7408 : 1.37749$. The percentage of silver in silver bromide thus incidentally determined is 57.446 against Stas's number 57.445.

Taking $\text{Ag} = 107.93$ and $\text{Br} = 79.955$, the atomic weight of barium is thus from the first ratio 137.426, with a maximum deviation of $+0.030$ and -0.040 from the mean; and from the second ratio 137.431, with a maximum deviation of ± 0.054 . Taking $\text{Ag} = 107.66$ and $\text{Br} = 79.955$, these numbers become 137.083 and 137.089 respectively. The difference between these numbers and those yielded by the older classical determinations is due partly to the improvements in analytical methods effected by Stas, and partly to improved methods of purification. J. N. W.

Copper Oxybromide analogous to Atacamite. By J. DUPONT and H. JANSEN (*Bull. Soc. Chim.* [3], 9, 193—195).—Brun (*Abstr.*, 1889, 1112) prepared an oxybromide of copper analogous to atacamite which appeared to form quadratic crystals, an observation which is surprising in view of the fact that atacamite crystallises in the orthorhombic system.

The authors prepare the oxybromide $\text{CuBr}_2 \cdot 3\text{CuO} + 3\text{H}_2\text{O}$ by heating a solution of cuprous bromide with copper oxide in a sealed tube at 200° , or, better, by heating neutral dilute solutions of cuprous bromide at 225° ; the green crystals obtained by the second method are found to be rhombohedral plates; their sp. gr. is 4.39. The constitution of atacamite and this compound is discussed, and from a study of their behaviour on heating (when they lose two-thirds of their water at 200° and the remainder at 250°), the authors submit, under reservation, the constitutional formulæ $\text{OH} \cdot \text{Cu} \cdot \text{O} \cdot \text{Cu} \cdot \text{Cl} + \text{H}_2\text{O}$ and $\text{OH} \cdot \text{Cu} \cdot \text{O} \cdot \text{Cu} \cdot \text{Br} + \text{H}_2\text{O}$ for atacamite and its bromine analogue.

A. R. L.

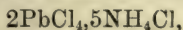
Metallurgy of Lead. By J. B. HANNAY (*Chem. News*, 67, 291).—It is found that, by simply melting and crystallising, all mixtures of lead and lead sulphide may be fractionated into metallic lead and lead monosulphide. This compound has, according to the author, a sp. gr. 7.766, and forms a series of volatile compounds with both carbonic anhydride, with carbonic oxide, with water, and with sulphurous anhydride, which are only stable at a red heat. The reaction $\text{PbS} + \text{PbSO}_4 = 2\text{Pb} + 2\text{SO}_2$ usually given as representing a reaction going on when lead is smelted in a reverberatory furnace is shown to be incorrect, inasmuch as when lead sulphide and lead sulphate react, the volatile compound PbS_2O_2 is formed. A minute study of the furnace reactions of lead and its oxide, sulphate, and sulphide has led to the conclusion that lead smelting is a fractionation of a low sulphide into lead and its sulphide with the formation of an oxysulphide, $\text{PbS} \cdot \text{PbO}$, which is the basis of black and grey slags. As a result of these investigations, a new metallurgy of lead has been devised in which the production of the slag-forming oxysulphide is avoided, and the volatile oxysulphide is utilised; whilst any silver can be eliminated, and any proportion of lead, its sulphate or oxide, can be formed directly from galena. During the fractionation of a low sulphide of lead into the metal and the monosulphide, a curious crystalline form of lead sulphide is produced. A new method of analysing lead sulphide has been devised by the author.

D. A. L.

Graphochemical Calculation. By E. NICKEL (*Zeit. physikal. Chem.*, 11, 598—607).—The author applies the method of calculation described in previous papers to the reactions involved in the reduction of lead ores.

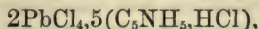
H. C.

Action of Liquid Chlorine on Metallic Chlorides. By A. CLASSEN and B. ZAHORSKI (*Zeit. anorg. Chem.*, 4, 100—110).—Compounds of lead tetrachloride have been prepared for the first time in the pure state. A solution of lead tetrachloride is obtained by digesting a mixture of the dichloride with liquid chlorine and fuming hydrochloric acid for 30—40 hours in a mixture of ice and salt. If ammonium chloride is added to this solution, a compound,



is obtained; it forms a lemon-yellow powder, turns orange when heated, and decomposes above 120° . It is decomposed by a small quan-

tity of water yielding lead dichloride, hypochlorous acid (and chlorine?), whilst with a large quantity of water, or with alkalis, it yields lead dioxide. If quinoline hydrochloride is used instead of ammonium chloride, a compound, $\text{PbCl}_4 \cdot 2(\text{C}_9\text{NH}_7 \cdot \text{HCl})$, is obtained. This has the same general characters as the ammonium compounds, but is more stable; with cooled solutions of bromide and iodide of potassium, it yields the bromide, $\text{PbBr}_4 \cdot 2(\text{C}_9\text{NH}_7 \cdot \text{HBr})$, as a red powder, and the iodide, $\text{PbI}_4 \cdot 2(\text{C}_9\text{NH}_7 \cdot \text{HI})$, as a brownish-black powder; these compounds decompose readily, and lose bromine or iodine respectively, when treated with alcohol and ether. A pyridine compound,



of a similar character was also prepared. Compounds of lead dichloride with pyridine hydrochloride, $3\text{PbCl}_2 \cdot 4(\text{C}_5\text{NH}_5 \cdot \text{HCl})$, and with pyridine, $3\text{PbCl}_2 \cdot 4\text{C}_5\text{NH}_5$, were prepared for the sake of comparison; they crystallise in colourless needles. Finally, it seems probable that a cobalt compound, $\text{Co}_2\text{Cl}_6 \cdot 10\text{C}_5\text{NH}_5 \cdot 2\text{CoCl}_2$, was obtained in the same way as the pyridine compound of lead tetrachloride.

C. F. B.

Mixed Double Haloids of Lead and Potassium. By C. H. HERTY (*Amer. Chem. J.*, 15, 357; compare Abstr., 1892, 779, and this vol., ii, 278).—The mixed double iodides and bromides of lead and potassium have been found (this vol., ii, 278) to be, as a rule, mixtures of the double salts $\text{KPbI}_3 \cdot x\text{H}_2\text{O}$ and $\text{KPbBr}_3 \cdot x\text{H}_2\text{O}$. When, however, the amount of lead iodide is made small in proportion to the bromide (less than 1 : 4 parts by weight), the crystals obtained from a solution of the two salts in a strong solution of potassium bromide (2 to 3 of water) contain at the most a trace of iodine, and have the formula $\text{K}_2\text{PbBr}_4 \cdot \text{H}_2\text{O}$. This salt has been previously obtained by Wells (*Amer. J. Sci.*, 45, 132), and is formed along with that of the formula $\text{KPbBr}_3 \cdot \text{H}_2\text{O}$, when lead bromide is dissolved, without the addition of bromine, in a strong solution of potassium bromide.

A. H.

Approximate Determination of the Equivalents of Earths by Titration. By G. KRÜSS and A. LOOSE (*Zeit. anorg. Chem.*, 4, 161—165).—The method consists in precipitating the rare earths by the addition of an excess of oxalic acid, filtering, and titrating the filtrate with potassium permanganate solution. It was proved that none of the oxalate remains in solution. The results obtained corresponded in every case with an equivalent higher than that obtained by conversion into sulphate in the ordinary way, and it is noted that in order to bring the two equivalents into agreement, it is necessary to multiply that obtained by titration by the factor $\frac{1}{17}$; the conclusion seems to be warranted that the cerium and yttrium earths form oxalates consisting of 17 equivalents of base combined with 16 equivalents of oxalic acid. There are difficulties to be overcome in obtaining confirmatory evidence of the above conclusion by direct analysis of the oxalates; these are being combated. It appears that in the case of the yttrium earths the oxalate approaches the normal in composition more nearly the greater the purity of the earth; on the

other hand, the tendency of the ytterbium earths is to form oxalates more basic than is represented by the ratio 17 : 16. The method may be useful for rapid determinations if the solution of the earth be not too acid, and the excess of oxalic acid used be reasonably small.

A. G. B.

Anhydrous Chlorides of Metals of the Rare Earths. By O. PETTERSSON (*Zeit. anorg. Chem.*, **4**, 1—9).—These were prepared by placing the mixture of oxides, obtained by working up a rare earth, in a tube of gas carbon, itself inclosed in a porcelain tube, and heating it to a white heat in a current of dry hydrogen chloride. Chlorides of the composition MCl_3 volatilise into the front part of the tube, and hydrogen and carbon monoxide are evolved; a small quantity of oxychloride and oxide remain behind. The carbon must act as the reducing agent, although it is only in contact, and not intimately mixed, with the oxide, for if the latter be placed in a platinum tube it is no longer reduced by hydrogen chloride. The chloride from nearly pure yttrium oxide forms a white, silky, laminated, crystalline mass; that from cerium oxide, a white powder; those from xenotime (a gadolinite mineral) and impure holmium oxide, a yellowish-grey, laminated mass. Of the metals of the gadolinite group, yttrium seems to form the most volatile chloride, of the cerite metals didymium, and the chlorides of the first-mentioned group seem to be in general more volatile than those of the second.

C. F. B.

Terbia. By K. HOFMANN and G. KRÜSS (*Zeit. anorg. Chem.*, **4**, 27—43).—That part of the mineral gadolinite which yields a yellow oxide, and has been supposed by Mosander, Delafontaine, Marignac, and De Boisbaudran to contain a distinct element, terbium, has been re-examined, the methods adopted including fractional decomposition of the nitrate by heat, fractional crystallisation of the formate and double sulphate, and fractional solution of the hydroxide in aniline hydrochloride (compare this vol., ii, 376). By this means it was shown that no fraction could be obtained with a definite atomic weight unalterable by further fractionation; hence the so-called terbia is not the oxide of a single element, but is a mixture of oxides. It is worthy of note that a fraction was obtained which could not be further decomposed by crystallisation of the double sulphate or formate, but which could yet be separated into fractions of different atomic weight by solution in aniline hydrochloride.

C. F. B.

Holmium Oxide. By K. HOFMANN and G. KRÜSS (*Zeit. anorg. Chem.*, **3**, 407—414).—The residual earth which remains after the separation of yttrium and scandium oxides from erbia has been shown by Cleve to consist of a less basic rose-coloured portion, and a more basic yellow portion, the solution of which shows absorption bands $\lambda = 640-2$ and 536, identical with those of Soret's holmium oxide, Ho_2O_3 , $Ho = 160$. Boisbaudran has shown that this portion is not a chemical individual, but is mixed with a more basic dysprosium oxide, whilst Crookes has further shown that the dysprosium oxide from gadolinite is itself complex, and contains holmium and other oxides. Krüss and Nilsson have arrived at a similar conclusion by a

comparative study of the spectra of the rare earths, and have found that holmium salts can be resolved into a series of fractions showing absorption bands varying in wave-length from $\lambda = 660.4$ to $\lambda = 428.5$.

To verify these views as to the complex nature of holmium oxide by gravimetric methods, the authors have now worked up and examined a considerable quantity of Nilsson's holmium material, consisting of oxide and of basic nitrate fractionally precipitated from the solution of the oxide. The various fractions all gave the holmium lines in exceptional strength, together with the erbium lines Er_α and Er_β , but their atomic weights varied from 139.1 to 163.6. The solution of the oxides was repeatedly fractionated with aniline hydrochloride, and eventually gave a series of identical fractions showing the holmium spectrum, and giving the atomic weight 161.6, closely agreeing with Cleve's 160. A similar preparation was made from the nitrates, and mixed with the first. The oxide thus prepared had a yellow colour, and turned white on heating with hydrogen, but without alteration of spectrum. It could not be further differentiated by fractional precipitation of the chloride with potassium sulphate, or by fractional decomposition of the nitrate by heat, so that apparently a chemical individual had been obtained. But by prolonged treatment with aniline hydrochloride, the oxide was split up into a series of fractions, in the less basic alone of which the holmium lines occurred, and the atomic weights obtained from these fractions formed a sinuous curve, which became more pronounced and at the same time more uniform in character as the fractionation proceeded, and pointed to the existence in the oxide of the two elements of atomic weights corresponding to the maxima and minima of the curves. The colour of the fractionated oxides inclined to red with increasing atomic weight. The atomic weight curve strongly resembled that yielded by erbia under similar treatment, but the constituent elements are not the same, for the absorption spectra were quite different. Moreover, the erbium oxides were obtained from feebly basic yttrium earths, whilst the holmium oxides were obtained from strongly basic yttrium earths containing a large amount of yttrium oxide. Whatever the relation may be between erbium and holmium oxides, the latter is undoubtedly a complex of two or more oxides of the yttrium group. JN. W.

Action of Heat on Zinc Permanganate. By T. KLOBB (*Bull. Soc. Chim.* [3], 9, 105—109).—Zinc permanganate, $\text{Zn}(\text{MnO}_4)_2 + 6\text{H}_2\text{O}$, when heated slowly, loses water and oxygen, and leaves zinc manganite. At 140° , the volume of oxygen evolved corresponds with the equation $2\text{Zn}(\text{MnO}_4)_2 = 2\text{ZnO} + 4\text{MnO}_2 + 3\text{O}_2$. Heated quickly, it gives off pink vapours or, more properly, a fine dust, of manganese trioxide. This substance was obtained by heating the permanganate in an open tube, aspirating the vapours formed through sulphuric acid containing a little anhydride, and then collecting them in a glass tube packed with fragments of porcelain; not more than 0.05 gram was obtained from 10—20 grams of the permanganate. The trioxide forms small, very hygroscopic lumps of a kermes colour; moisture

colours it reddish-violet, and it decomposes at 60° , leaving a brown residue. It may be kept unchanged for a long time in a sealed tube. A determination of the metal and of the available oxygen corresponded roughly with the formula MnO_3 . C. F. B.

Reduction of Ferric Salts and Solution of Ignited Ferric Oxide. By L. STORCH (*Chem. Centr.*, 1893, i, 876; from *Ber. Österr. Ges. Chem. Ind.*, 15, 9—13).—The author has investigated the action of zinc on ferric sulphate under various conditions, as he believes that the reduction is due to the direct action of the zinc and not to nascent hydrogen. In all cases considerable excess of zinc was necessary, and the action proceeded slowly. Copper in the form of thin wire gives much better results.

Ignited ferric oxide readily dissolves on warming with sulphuric acid (40 per cent.). J. B. T.

Iron Chloroborate and Chloroborates Isomorphous with Boracite. By G. ROUSSEAU and H. ALLAIRE (*Compt. rend.*, 116, 1195—1197).—Chloroborates isomorphous with boracite are obtained by the action of the vapours of metallic chlorides on native calcium borate or, better, on boronatrocalcite. As a rule, crystalline products cannot be obtained by the fusion of calcium borate with chlorides.

The case of iron presents special difficulties, because ferrous chloride is not volatile at a sufficiently low temperature. Good results are, however, obtained by passing the vapour of ferric chloride over an intimate mixture of calcium borate with a large excess of small pieces of wrought iron or steel wire, the mixture being heated at about 330° . Ferrous chloride is formed, and immediately reacts with the borate. The excess of ferrous chloride is dissolved by means of water, and the unattacked iron is easily separated. The product has the composition $6FeO, 8B_2O_3, FeCl_2$, a small portion of the iron being replaced by isomorphous calcium.

Iron chloroborate crystallises in greyish, transparent cubes, which act on polarised light. Natural boracite has similar special properties, and the symmetry is really pseudo-cubic. The iron compound dissolves slowly in nitric acid, and is rapidly decomposed by fused alkali carbonates.

Zinc chloride and cadmium chloride also yield pseudo-cubic boracites. C. H. B.

Cobalt. By E. DONATH (*Monatsh.*, 14, 93—108).—Pure unoxidised cobalt does not dissolve in strong, hot aqueous potash; the blue solution obtained under these circumstances with finely-divided cobalt, reduced from the oxide, is due to oxide still admixed with the metal. This blue solution does not, as several observers have stated, contain cobalt in any higher state of oxidation than that corresponding with CoO , for it does not liberate iodine from an acid solution of potassium iodide, nor does it oxidise an acid solution of ferrous ammonium sulphate. If the blue solution be allowed to remain in contact with air, it can be shown to absorb oxygen, and the dark substance which separates out has a composition intermediate between

Co_3O_4 and Co_2O_3 . But since this was formed by oxidation of the substance present in the blue solution, the latter must be in a lower state of oxidation, and thus cannot possibly be CoO , as several observers have supposed. C. F. B.

The Elementary Nature of Nickel and Cobalt; their Atomic Weights. By C. WINKLER (*Zeit. anorg. Chem.*, **4**, 10—26).—The grounds are first discussed on which Krüss and Schmidt (*Abstr.*, 1889, 349, 1114; this vol., ii, 212) and Remmler (this vol., ii, 211) base their conclusions that nickel and cobalt, as hitherto known, are not pure elements, and it is suggested that the variations in the atomic weights noticed by these observers were due to impurities derived from the glass vessels used. The author concludes, "I cannot believe that nickel contains a hitherto unknown substance, differing from it in properties and atomic weight; on the contrary, I regard both it and cobalt as simple substances, and elements in the present sense of the word."

The atomic weights of both elements were determined by dissolving a weighed quantity of the metal, purified by two successive electrolytic depositions in hydrochloric acid in a platinum basin, evaporating to dryness, heating the residual chloride at 150° , and estimating the chlorine in it, in one series gravimetrically, in another volumetrically by Volhard's method, six determinations being made by each method. Results: Ni = 58.8334—58.9684, mean 58.90; Co = 59.5996—59.7480, mean 59.67. [Standard not given.] The mean values are probably more accurate than the divergence of the individual results indicates. C. F. B.

Reactions with Ammonia at Low Temperatures. By O. T. CHRISTENSEN (*Zeit. anorg. Chem.*, **4**, 227—233).—Regarding the function of ammonia in the metallic ammonium compounds as similar to that of water in crystalline salts, the author argues that salts which will not combine with ammonia at ordinary temperatures should do so at low temperatures, just as salts which are anhydrous at ordinary temperatures become hydrated at low temperatures.

When liquid ammonia is brought into a beaker containing anhydrous, violet chromic chloride, cooled in a mixture of solid carbonic anhydride and ether to about -75° , there is no reaction. But when the vessel is removed from the freezing mixture, and the temperature allowed to rise nearly to the boiling point of the ammonia, a violent reaction ensues, the chromic chloride being converted into a red mass. After the odour of ammonia has nearly disappeared, the mass is washed with cold water (whereby a portion of it is dissolved with a yellow colour) until the washings show the colour of chloropurpureochromium chloride; the undissolved residue is then treated with concentrated hydrochloric acid, the acid poured off, and the still undissolved residue washed on a filter, and finally dissolved in cold water. This solution is poured into strong hydrochloric acid, whereby pure chloropurpureochromium chloride is precipitated.

The yellow, aqueous washings mentioned above yield luteochromium nitrate on the addition of strong nitric acid.

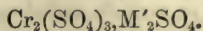
The reaction between chromic chloride and ammonia is much retarded by the presence of water, and only occurs at temperatures of a comparatively narrow range, the boiling point of ammonia being apparently the most favourable temperature.

When ferric chloride is treated with liquid ammonia, a reddish-yellow powder is obtained which is immediately decomposed by water.

Red potassium chromium chloride also yields a mixture of chromammonium compounds when treated with liquid ammonia.

A. G. B.

Chromodisulphuric, Chromotrisulphuric, and Chromosulphochromic acids. By A. RECOURA (*Compt. rend.*, 116, 1367—1370).—Under the name of chromosulphates, the author has previously described (Abstr., 1892, 783) compounds of the type



Chromosulphuric acid is most easily prepared by evaporating on a water-bath a solution containing violet chromium sulphate and sulphuric acid in molecular proportion, and heating the residue at 110—120°.

Chromodisulphuric acid, $(\text{Cr}_2\text{SO}_4)_4\text{H}_4$, and chromotrisulphuric acid, $(\text{Cr}_2\text{SO}_4)_6\text{H}_6$, are obtained in a similar way, using 2 or 3 molecular proportions of sulphuric acid.

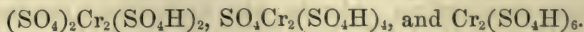
The three acids are deep green powders soluble in water in all proportions. They are quite stable in the solid condition, but gradually decompose in solution. Dilute barium chloride solution produces a greenish-white, flocculent precipitate of barium chromosulphate, but a concentrated solution of barium chloride yields a precipitate of barium sulphate. Their heats of neutralisation are greater than that of sulphuric acid.

$(\text{Cr}_2\text{SO}_4)_4\text{H}_4$	diss. + 2NaOH diss. ...	develops	+ 33·3 Cal.
$(\text{Cr}_2\text{SO}_4)_5\text{H}_5$	„ + 4NaOH „ ...	„	+ 33 × 2 Cal.
$(\text{Cr}_2\text{SO}_4)_6\text{H}_6$	„ + 6NaOH „ ...	„	+ 32 × 3 „
SO_4H_2	„ + 2NaOH „ ...	„	+ 30·8 Cal.

The energy of the acid function decreases as the proportion of sulphuric acid increases.

The chromosulphates are obtained by evaporating a solution of chromic sulphate with 1, 2, or 3 molecular proportions of the particular sulphate. They are soluble in water, and their solutions are more stable than those of the free acids. Dilute barium chloride solution produces no precipitate.

The constitution of the three acids is most probably



Chromosulphochromic acid, $\text{Cr}_2\text{SO}_4\text{CrO}_4\text{H}_2$, can be obtained by the combination of chromic sulphate with chromic acid. If the constitution attributed to the chromosulphates be correct, the constitution of this acid will be $(\text{SO}_4)_2\text{Cr}_2 < \begin{smallmatrix} \text{SO}_4\text{H} \\ \text{CrO}_4\text{H} \end{smallmatrix}$, and this view is supported by

the fact that the heats of neutralisation of the two acid functions are respectively 16.0 Cal. and 12.3 Cal.

C. H. B.

Sodium Perchromate. By C. HAÜSSERMANN (*J. pr. Chem.* [2], 48, 70—72).—A salt of the composition $\text{Na}_6\text{Cr}_2\text{O}_{15} + 28\text{H}_2\text{O}$ crystallises after some time from a solution made by adding sodium peroxide to a thin paste of chromium hydroxide and water, kept at 10—20°. It forms red-brown, vitreous crystals which rapidly effloresce in the air. In dilute sulphuric acid they are rapidly decomposed, with evolution of oxygen and formation of chromium sulphate, but there is an intermediate development of the characteristic blue colour of perchromic acid. By treatment with hot water, a part of the sodium is converted into sodium hydroxide, the remainder becoming sodium chromate. The analytical numbers indicate the equation $\text{Na}_6\text{Cr}_2\text{O}_{15} + \text{H}_2\text{O} = 2\text{Na}_2\text{CrO}_4 + 2\text{NaOH} + 3\text{O}_2$ as representing the change. The author is investigating the question of the constitution of the anhydride, Cr_2O_{12} , corresponding with this salt.

A. G. B.

Preparation of Tungsten, Molybdenum, and Vanadium in the Electric Furnace. By H. MOISSAN (*Compt. rend.*, 116, 1225—1227).—The oxides of tungsten, molybdenum, and vanadium, metals which have hitherto proved very difficult to isolate and obtain in a fused condition, were intimately mixed with carbon, and heated in the electric furnace (this vol., ii, 167).

With a current of 350 ampères and 70 volts, an ingot of 120 grams of tungsten is obtained in about 10 minutes, and if the oxide has been present in excess, the metal is pure. It is brilliant, and very hard; sp. gr. = 18.7. If, on the other hand, the carbon is in excess, products are obtained containing a proportion of carbon which varies with the conditions from 0.64 to 6.33 per cent. These products have a brilliant fracture, are stable in presence of air, and are sometimes covered with a layer of blue tungsten oxide. At a much higher temperature (with a current of 1000 ampères and 70 volts), the proportion of carbon in the product rises to 17.27—18.81 per cent.

Molybdenum oxide, obtained by heating ammonium molybdate, yields a molybdenum carbide containing 9.77—9.90 per cent. of carbon. It has a brilliant fracture, is very hard, and scratches steel and glass, and remains unaltered in moist air; sp. gr. 8.6.

Vanadium oxide is only very slightly reduced with a current of 350 ampères and 70 volts; but with a current of 1000 amperes and 70 volts it is rapidly reduced, and yields a carbide containing as much as 25 per cent. of carbon (17.56 to 25.68); sp. gr. = 5.3.

It would seem that the higher the temperature the greater the proportion of carbon taken up. It also seems that molybdenum, uranium, tungsten, and vanadium are less fusible than chromium, their fusibility following the order given.

C. H. B.

Action of Hydrogen Haloids on Molybdic acid. By E. F. SMITH and V. OBERHOLTZER (*Zeit. anorg. Chem.*, 4, 236—246).—When molybdic acid is heated at 150—200° in hydrogen chloride, the com-

compound $\text{MoO}_3 \cdot 2\text{HCl}$ is sublimed (Debray, *Compt. rend.*, **46**, 1098). When hydrogen bromide is substituted for the chloride, a compound, $\text{Mo}_2\text{O}_3\text{Br}_4$, sublimes in the form of square, permanganate-coloured plates which are unstable in air; at the same time a brownish-yellow liquid, $\text{MoO}_3 \cdot 3\text{HBr}$, condenses in the tube, and crystallises in long, yellow, deliquescent needles when cold.

Hydrogen iodide begins to act on molybdic acid in the cold, iodine being liberated, and a violet-coloured substance formed, the composition of which could not be accurately ascertained. At $105-120^\circ$ the product retains no iodine, and consists of the oxide, $\text{Mo}_4\text{O}_{10} \cdot 3\text{H}_2\text{O}$, which is blue, and stable in air.

Hydrogen fluoride, at $300-400^\circ$, converts molybdic acid into a volatile, white, crystalline oxyfluoride, $\text{Mo}_2\text{O}_3\text{F}_4$; it is deliquescent, and easily soluble in hydrofluoric acid, but not in water. Indications of other products were obtained.

A. G. B.

Phosphomolybdates. By C. FRIEDHEIM (*Zeit. anorg. Chem.*, **4**, 275—297; compare this vol., ii, 282).—The author reviews our knowledge of the constitution of the so-called phosphomolybdic acid and its salts. By the interaction of potassium dihydrogen phosphate and molybdic anhydride, there are produced several white compounds, which may be regarded as molecular aggregates of the micro-crystalline salt, $\text{K}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 2\text{MoO}_3 + 13\text{H}_2\text{O}$, produced at a certain stage of concentration, with potassium molybdate.

When fewer than two molecular proportions of molybdic anhydride react with one of potassium monohydrogen phosphate, the compounds $5\text{K}_2\text{O} \cdot 2\text{P}_2\text{O}_5 \cdot 10\text{MoO}_3 \cdot 11\text{H}_2\text{O}$ and $3\text{K}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 5\text{MoO}_3 \cdot 7\text{H}_2\text{O}$ are produced. When two molecular proportions of the anhydride are used, the compounds $5\text{K}_2\text{O} \cdot 2\text{P}_2\text{O}_5 \cdot 10\text{MoO}_3 \cdot 20\text{H}_2\text{O}$; $2\text{K}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 4\text{MoO}_3 \cdot 8\text{H}_2\text{O}$; and $\text{K}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 5\text{MoO}_3 \cdot 6\text{H}_2\text{O}$ are formed.

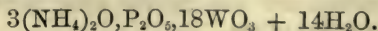
Potassium phosphate reacting with molybdic anhydride in the proportion of $1\text{P}_2\text{O}_5 : 5\text{MoO}_3$ gives rise to the compounds $3\text{K}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 5\text{MoO}_3$; $5\text{K}_2\text{O} \cdot 2\text{P}_2\text{O}_5 \cdot 10\text{MoO}_3$; $2\text{K}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 5\text{MoO}_3$; $2\text{K}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 4\text{MoO}_3$.

The author discusses the constitution of these compounds, and describes the isolation of the sodium compounds

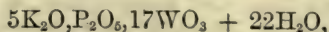
$3\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 18\text{MoO}_3 \cdot 26\text{H}_2\text{O}$; $5\text{Na}_2\text{O} \cdot 2\text{P}_2\text{O}_5 \cdot 48\text{MoO}_3 \cdot 100$ (or 111) H_2O ; and $3\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 18\text{MoO}_3 \cdot 25\text{H}_2\text{O}$.

A. G. B.

Phospholuteotungstic acid. By F. KEHRMANN (*Zeit. anorg. Chem.*, **4**, 138—144).—It was found desirable, for certain reasons, to revise the work (Abstr., 1887, 777) on this acid. The acid has been found to have the composition $\text{P}_2\text{O}_5 \cdot 18\text{WO}_3 + 41\text{H}_2\text{O}$; the potassium and ammonium salts are $3\text{K}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 18\text{WO}_3 + 14\text{H}_2\text{O}$ and



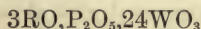
When the potassium salt is treated with potassium hydrogen carbonate at the ordinary temperature, it yields a compound



in white, satiny needles; from the ammonium salt, a compound may also be obtained, in tabular crystals, by the action of ammonium hydrogen carbonate; in it the ratio $P_2O_5 : WO_3$ also = 1 : 17.

The estimation of potassium in the salts of these complex acids is conveniently effected by precipitating the acid with a solution of an organic base, especially quinoline, in an acid, such as acetic, sulphuric, or hydrochloric, and determining the potassium in the filtered solution.

As a result of the comparison of many phospho- and arsenotungstates and -molybdates, it seems that salts belonging to the four classes $3RO, P_2O_5, 18MoO_3$, $3RO, As_2O_5, 18MoO_3$, $3RO, P_2O_5, 18WO_3$, and $3RO, As_2O_5, 18WO_3$ must possess a similar structure, as also those of the three classes $3RO, P_2O_5, 24MoO_3$, $3RO, As_2O_5, 24MoO_3$, and



(water of crystallisation is omitted in these formulæ). C. F. B.

Preparation of Zirconium and Thorium. By L. TROOST (*Compt. rend.*, 116, 1227—1230).—An intimate mixture of zirconium oxide and carbon, when heated in the electric arc in an atmosphere of carbonic anhydride, yields small, metallic masses, which contain 76·9 to 78·2 per cent. of zirconium and 23·1 to 21·8 per cent. of carbon, and which, therefore, approximate closely in composition to zinc carbide, ZnC_2 . The product is steel-grey in colour, and is very hard, scratching glass easily, whilst it is itself unaffected by the hardest steel. If the cupel is brasqued with zirconium oxide, the proportion of carbon in the product is lower. The carbide is readily dissolved by hydrofluoric acid, even when dilute, but it is not attacked by other acids. If the proportion of carbon is low, it only oxidises superficially at a red heat, but it burns brilliantly at this temperature if it contains a high proportion of carbon. With the current used (30 to 35 ampères and 70 volts), no volatilisation of zirconium was observed. If, however, zircon is heated in the arc, silica volatilises, and condenses in long filaments.

Thorium oxide, under similar conditions, is reduced more easily than zirconium oxide, and the product contains 8·2 to 9·5 per cent. of carbon, and, therefore, approximates in composition to the carbide, ThC_2 . It is less hard than the zirconium carbide, is very brittle, and scratches glass slightly; sp. gr. at $15^\circ = 10\cdot15$. It decomposes cold water, with evolution of hydrogen mixed with strongly smelling hydrocarbons, and it gradually decomposes with intumescence when exposed to moist air. At a red heat it burns rapidly and brilliantly.

If this carbide is heated in the arc with excess of thorium oxide, it yields small, metallic masses, which do not alter when exposed to air.

C. H. B.

Black Antimony Trisulphide. By C. A. MITCHELL (*Chem. News*, 67, 291).—By dissolving 5 grams of antimony trioxide in 30 c.c. of a mixture of 2 parts of hydrochloric acid and 1 of water and saturating the solution with hydrogen sulphide, then keeping it boiling while a current of carbonic anhydride is passing through, a portion of the orange sulphide dissolves, but some is precipitated as

black sulphide; by repetitions of the treatment, all the sulphide ultimately assumes the latter form, which has the composition Sb_2S_3 .

D. A. L.

Double Halogen Compounds of Gold. By E. PETERSEN (*J. pr. Chem.* [2], 48, 88—91).—The author maintains, in reply to Krüss and Schmidt (this vol., ii, 284), that the product of the action of chlorine, or of bromine, on gold is neither a mixture of gold and a trihaloid, nor of a mono- and tri-haloid, but a true aurosoauric haloid.

A. G. B.

Action of Chlorine and Bromine on Gold. By G. KRÜSS and F. W. SCHMIDT (*Zeit. anorg. Chem.*, 3, 421—427).—A reply to Thomsen (this Journal, 1877, ii, 485; Abstr., 1888, 559) and Petersen (this vol., ii, 126). A repetition of Thomsen's experiment on the direct chlorination of precipitated gold shows that considerably more chlorine (29.0 per cent.) is taken up than that required by the formula Au_2Cl_4 (26.5 per cent.). Petersen's results (in five different preparations, 25.7—29.1 per cent. of chlorine) indicate that he was dealing with a mixture of variable composition. On repeating his experiment, the authors find that the residue left after exhausting the product of chlorination with alcohol contains chlorine (15.96 per cent.), closely corresponding with that contained in aurous chloride (15.24 per cent.). The action of bromine on precipitated gold (5.5 grams), under Thomsen's conditions, has been further studied, with specially purified materials, with the result that the weight of the product (12.08 grams) corresponds with the weight of auric bromide (12.19 grams) required by theory. The product, moreover, is practically entirely soluble in water.

Jx. W.

Action of Silicon on Gold, Silver, Platinum, and Mercury. By H. N. WARREN (*Chem. News*, 67, 303—304).—A brittle regulus, fusible at a red heat, having a crystalline fracture, only slightly soluble in acids, and containing 10 per cent. of silicon, is obtained when graphitoid silicon is heated to a full red heat in contact with platinum, or when a mixture of amorphous silicon and platinum-black is heated under a layer of potassium silicofluoride in a closed crucible. By heating to a high temperature a mixture of potassium silicofluoride, sodium, and amorphous gold or silver, a silicide of the metal may be obtained. These metals alone will not combine directly with silicon, but, if in the molten state they are contaminated even with only a small quantity of the silicide obtained in the manner just described, a considerable amount of elementary silicon is readily absorbed. Silver containing 5 per cent. of silicon is as brittle as antimony, and looks like a highly argentiferous alloy of gold and silver, and when the proportion of silicon is raised to 10 per cent., silver silicide becomes slightly red, and resembles metallic manganese in appearance; when pulverised, the regulus is completely decomposed by concentrated hydriodic acid. When mercury in contact with an alcoholic solution of silicon fluoride was submitted to the action of a powerful battery, the mercury, when subsequently distilled, left a residue of a small quantity of amorphous silicon, but no silicide of mercury was isolated.

D. A. L.

Palladium Sulphides. By P. PETRENKO-KRITSCHENKO (*Zeit. anorg. Chem.*, **4**, 247—250).—The palladium sulphide prepared by precipitating a palladous salt with hydrogen sulphide always contains more sulphur than corresponds with the formula PdS . Attempts to produce this sulphide by heating potassium palladium chloride in hydrogen sulphide resulted in mixtures of the sulphides PdS_2 and Pd_2S . The author concludes that there is no certain evidence of the existence of the sulphide PdS . A. G. B.

Mineralogical Chemistry.

Iron from Ovifak. By H. MOISSAN (*Compt. rend.*, **116**, 1269—1271).—Several specimens of the iron from Ovifak were examined for the various forms of carbon, in the manner previously described. In one specimen, fragments of sapphire were found. Three specimens contained amorphous carbon, two of them contained intumescent graphite, one alone contained ordinary graphite, and none of them contained diamonds in any form. C. H. B.

Occurrence of Gold containing Palladium in the Caucasus. By T. WILM (*Zeit. anorg. Chem.*, **4**, 300—302).—A gold matte from a sand rich in magnetic iron ore, from the neighbourhood of Batoum, was found to contain 8—9 per cent. of palladium. The chemical interest of the occurrence resides in the fact that the palladium is not converted into palladous chloride when the aqua regia solution of the palladiferous gold is evaporated and treated with hydrochloric acid, the presence of the gold apparently hindering the reduction. The usual indication of the presence of palladium, the red-brown colour of palladous chloride solution, being thus unattainable, this metal is liable to be qualitatively mistaken for platinum when it occurs in gold, the more so because the ammoniopalladic chloride, into which it is converted by the usual treatment with ammonium chloride, much resembles impure ammonioplatic chloride. A. G. B.

Physiological Chemistry.

Influence of Carbonic Anhydride on the Diastatic and Peptone-forming Ferments in the Animal Organism. By N. P. SCHIERBECK (*Chem. Centr.*, 1893, i, 745—746; from *Skandinav. Arch. Physiol.*, **3**, 343).—The action of human saliva on various starches is increased by the presence of carbonic anhydride, except in the case of wheat-starch, which, however, behaves like the others if made slightly alkaline. In presence of acids, carbonic anhydride

either hinders or entirely prevents the fermentation. Similar results were observed in the case of invert ferment solution with cane sugar, of saliva with glycogen, and of pancreas extract with rice starch; the larger the quantity of alkali present, the greater the proportion of carbonic anhydride required to accelerate the action.

Animal diastatic ferments react most readily in acid solution, for the acidification of which hydroxypropionic acid is preferable to hydrochloric acid; the presence of 5—10 per cent. carbonic anhydride is sufficient in these cases also to hinder the fermentation. Similar results were observed with trypsin. Saliva and pancreas ferment containing trypsin, unlike pepsin, are not decomposed by carbonic anhydride; its effect on the course of the fermentations appears to be due to the acidity it produces. J. B. T.

Metabolism in a Child 14 Months old. By W. CAMERER (*Zeit. Biol.*, 29, 227—232).—Observations on the metabolism of young children are difficult on account of the collection of urine and fæces. In the present experiment on a girl these difficulties appear to have been successfully overcome.

The experiment lasted four days. The diet was simple, consisting of milk, egg, biscuit, and water.

The amount of proximate principles may be stated thus in grams per diem :—

	Mean.	Minimum.	Maximum.
Water	1191.0	970.0	1389.0
Proteid	31.0	25.0	38.6
Fat	21.4	17.3	27.2
Carbohydrate....	126.0	118.0	133.0

The analyses of urine are given in the following table :—

Urine.	Quantity.	Total N.	Hüfner N.	N residue.	Urea by Hüfner's method.	Uric acid by different methods.	Nitrogen in xanthine substances.
	grams	grams	grams	grams	grams	milligrams	milligrams
Of the 1st and 2nd days }	850	3.47	3.15	0.32	6.755	160 to 173	3.5
Of the 3rd and 4th days }	660	4.07	3.65	0.41	7.833	149 to 166	3.1
Mean of the 4 days }	755	3.77	3.40	0.37	7.284	155 to 169	3.3

Taking the mean of the four days, and the total nitrogen as 100,

the nitrogen residue was 9·8, that of the uric acid 1·4, and that of the xanthine substance 0·09. Taking the urea as 100, the uric acid is a little over 2.

The small output of uric acid is noteworthy; the same was found in earlier researches in children of from 2 to 5 years of age.

W. D. H.

Metabolism during Inanition. By W. PRAUSNITZ (*Zeit. Biol.*, 29, 151—167).—Fifteen experiments on adult human beings are recorded in which the nitrogenous excretion was estimated during a period of inanition lasting two days. The output of nitrogen is, of course, diminished in comparison with the normal; but the chief point of interest noted is that, on the second day, the output is either practically the same as on the first, or more frequently (12 out of the 15 experiments) exceeds it—often very considerably.

The following table gives the amount of nitrogen in grams:—

Experiment.	Normal days.	First hunger day.	Second hunger day.
1	9·3 to 11·7	7·8	13·0
2	64 to 81 (? 6·4 to 8·1)	4·6	4·4
3	16·8	11·9	10·6
4	12·2	9·6	13·0
5	9·6 to 12	13·3	11·0
6	7·8 to 8·5	7·9	10·3
7	—	9·3	12·5
8	14·2 to 15·3	14·0	14·9
9	18·6	12·9	13·8
10	15·5 to 16·2	7·9	14·5
11	12·4	7·7	12·6
12	15·8 to 16·9	13·3	16·0
13	13·6 to 13·9	8·2	14·9
14	—	11·7	13·0
15	22·3 to 23·1	17·3	19·3

W. D. H.

Physiology of Starvation. By C. LEHMANN, F. MUELLER, I. MUNK, H. SENATOR, and N. ZUNTZ (*Virchow's Archiv*, 131, Suppl. No., 1—228).—Two very complete series of observations are recorded on two individuals who submitted themselves for experiment. In the first case, the well-known professional faster, Cetti, was starved for 10 days. In the second, a young German, named Breithaupt, was the subject of an experiment which lasted for six days. In both cases water was allowed.

The facts observed come under the following headings: (1) general condition, including exhaustive measurements of the various parts of the body; condition of pulse, with tracings; blood corpuscle counting, and body weight; (2) examination of the fæces and urine; and (3) respiratory exchange.

Observations were made daily, and the results are given in detail, and also tabulated. References are also given to other work of a similar kind, especially to Luciani's work on Succi, when the general results were much the same.

The chief facts noted are as follows:—

Weight—Cetti weighed 57 kilos. at the beginning, and 50·6 kilos. at the end of the hunger period. The loss of weight was most marked during the first half of this period. Breithaupt weighed 60 kilos. at the beginning, and 56·5 kilos. at the end of his experiment. The body measurements showed a gradual diminution in each case, and was most marked in situations where large masses of muscle and fat were present.

Circulation.—The frequency of the pulse was in Cetti's case but little altered, but arterial tension was lessened, as shown by the sphygmograph. Breithaupt's pulse became very slow (on the sixth day 47): the pulse curve, however, showed less alteration than in Cetti's case. In both cases the excitability of the heart was increased, slight exertion sending up the pulse rate. Examination of the blood showed, in the case of Cetti, a rise in the number of red and white corpuscles, but a fall in the amount of hæmoglobin. In Breithaupt's case there was a slight rise in the number of corpuscles, and in the amount of hæmoglobin also.

Fæces.—As compared with dogs and cats, the amount was small; the nitrogen in it was relatively larger than normal, although the absolute amount was small. Fat and fatty acids were abundant. The odour denoted very little putrefaction. Hydrobilirubin was present, mixed with bilicyanin.

Urine.—The quantity of urine varied with the amount of water drunk; its specific gravity was in the inverse ratio. The acidity of the urine was increased. The nitrogen excreted was diminished, but only to a small extent. This appears to be one of the most striking points noticed in the investigation. From this the amount of proteid metabolism was estimated: the amount of proteid decomposed daily in Cetti's case varying from 56 to 95 grams; in Breithaupt's case from 62 to 80 grams. The excretion of sulphur ran parallel to that of nitrogen. The quotient A/B (A = preformed sulphuric acid, B = combined sulphuric acid) varied in the two cases considerably. Acetone and phenol were present in considerable quantity; and traces of albumin were found in both cases; indican was absent.

The amount of chlorides sank very greatly; that of phosphates did not; and this, combined with the fact that calcium and magnesium were but little affected, suggests that the bones underwent wasting; the amount of phosphate and calcium being too great to be accounted for by muscular wasting. The amount of sodium excreted was very small, less than that of potassium.

Respiratory Exchange.—This is most carefully and exhaustively given; and again one is struck with the very small variations from the normal condition. The temperature also remained constant. The influence of work was difficult to investigate because of the early onset of fatigue, especially of the heart. But the small increase of the respiratory quotient during work excludes the possibility that carbohydrate material can be an important source of muscular power.

W. D. H.

Proteïds of Nervous Tissues. By W. D. HALLIBURTON (*J. Physiol.*, 15, 90—107).—The normal reaction of nervous tissues is

alkaline. This alkalinity diminishes after death, and may be replaced by an acid reaction. This is most marked in the region where there are most cells, namely, in the grey matter.

Quantitative determinations show that proteid matter is a very important constituent of nervous structures. The average amount of proteid in the solids of grey matter is over 50 per cent. It is less in the white matter, and also in parts like the spinal cord, which contain large quantities of white matter. It is less still in nerve. Grey matter is also the poorest in total solids; nerve the richest. In any region like the spinal cord, where there is a mixture of white and grey matter, the percentage of water, the proportion of proteid in the solids, and the proportion of grey matter vary directly the one with the others.

The following table gives a summary of a number of analyses which illustrate this point:—

	Water.	Solids.	Percentage of proteid in solids.
Grey matter of cerebrum.....	83·5	16·5	51
White " "	70·0	30·0	33
Cerebellum.....	80·0	20·0	42
Spinal cord as a whole	72·0	28·0	31
Cervical region of cord.....	72·5	27·5	31
Dorsal " "	70·0	30·0	28
Lumbar " "	73·0	27·0	33
Sciatic nerves.....	61·0	29·0	29

Qualitative examination of this proteid matter shows that the proteids present are three in number, A, B, and C.

A. This proteid is a globulin, and may be termed neuro-globulin α . It is coagulated by heat at the low temperature of 47°, and is analogous to similar globulins obtained from other cellular structures. It is precipitated by a comparatively small percentage of such neutral salts as magnesium sulphate; it is not precipitated by weak acetic acid, and contains no phosphorus in its molecule.

B. This proteid is a nucleo-albumin. It can be readily obtained by precipitating an aqueous extract of brain with weak acetic acid. The supply obtainable from white matter is small. It is coagulated by heat at 56—60°. It is precipitable by saturating its solutions with neutral salts. It contains 0·5 per cent. of phosphorus. After subjection to gastric digestion, an insoluble residue of nuclein remains behind. Dissolved in dilute sodium carbonate solution, and injected into the circulation of rabbits, it causes extensive intravascular coagulation.

C. This proteid is a globulin, and may be termed neuro-globulin β . It is coagulated by heat at 70—75°. It requires complete saturation with magnesium sulphate to precipitate it entirely. Peptone, proteose, myosin, albumin, and fibrin-ferment (in Schmidt's sense) are not obtainable from nervous tissues.

W. D. H.

Action of Sodium Oxalate on Voluntary Muscle. By F. S. LOCKE (*J. Physiol.*, 15, 119—120).—A frog's sartorius, immersed in 0.75 sodium oxalate solution, becomes in a few seconds violently active, much more so than in Biedermann's "normal saline" solution. After 30 to 45 minutes, it loses its irritability, which, however, is partially recovered by immersion in 0.6 sodium chloride solution made with New River water.

This probably explains the symptom of fibrillary muscular contraction observed by Kobert and Küssner in sodium oxalate poisoning, and which they ascribed to an action on the central nervous system.

W. D. H.

Phloridzin Diabetes. By W. PRAUSNITZ (*Zeit. Biol.*, 29, 168—174).—Two experiments on dogs are recorded; in each, two similar animals were used. In one, the glycogen of the body was estimated; in the other, phloridzin diabetes was produced. The amount of sugar extracted was in great excess beyond what the glycogen in the control animal would account for. The phlorose arising from the drug would only account for quite a small percentage of the sugar excreted.

W. D. H.

Phloridzin Diabetes in Frogs. By M. CREMER (*Zeit. Biol.*, 29, 175—176).—Phloridzin given subcutaneously produces diabetes in frogs. The sugar in the urine gave Trommer's test, and yielded crystals of phenylglucosazone.

W. D. H.

Phloridzin Diabetes. By M. CREMER and A. RITTER (*Zeit. Biol.*, 29, 256—276).—From experiments on rabbits recorded in the present paper, and from the consideration of the work of others in the same direction, the question of the origin of the sugar produced by phloridzin is discussed. The glycogen of the body will not account for it; the sugar derived from the drug itself is also insufficient: indeed, phloridzin appears to be wholly excreted as such in the urine. Its presence renders polarimetric estimation of the sugar in the urine untrustworthy as phloridzin is lævorotatory. Further, the possible origin of the sugar or a part of it from the chondrosin of cartilage and from glucosamine is discussed, but the conclusion is arrived at that the only satisfactory explanation is that the sugar arises from the proteid of the body. This view is confirmed in a very striking way by tables and charts, which show that the proteid metabolism in phloridzin diabetes, as in pancreatic diabetes, runs parallel to the amount of sugar excreted. The curves of nitrogen output and sugar excretion rise and fall one with the other.

W. D. H.

Urinary Hæmatoporphyrin. By A. E. GARROD (*J. Physiol.*, 15, 108—118).—In continuation of previous researches (Abstr., 1892, 1506), it is found that hæmatoporphyrin can generally be detected in urine; in normal urine its quantity is very small. Direct spectroscopic examination of specimens rich in hæmatoporphyrin shows that it is alkaline hæmatoporphyrin which is present.

When neutral hæmatoporphyrin is added to urine, the spectrum seen is that of the alkaline pigment, even though the urine is acid, or even

though it is made considerably more acid than normal by the addition of acid sodium phosphate. If, however, large excess of this phosphate is added, the acid spectrum appears.

Amyl alcohol extracts the pigment from urine, but it is mixed with urobilin and uroerythrin. Ethylic acetate and carbon tetrachloride also take up the pigment; chloroform only dissolves traces. In all cases it is the alkaline pigment which is obtained, but this sometimes shows an additional (fifth) band far into the red: the same is occasionally seen in the urine itself.

Some specimens deepen in tint on standing; hence the supposition that urinary hæmatoporphyrin may partially exist as a chromogen.

In some cases hæmatoporphyrin is obtainable from sediments of urates; and in other cases a pigment is obtained which appears to be a precursor of hæmatoporphyrin. Its absorption bands are similar to those of oxyhæmoglobin; it is identical with the substance obtained when hæmatoporphyrin is treated with zinc chloride and ammonia. It is unchanged by alkalis, but is at once changed into hæmatoporphyrin by mineral acids. It appears to be identical with a similar pigment isolated by Stockois by dialysis from the urine of one of his cases, and also noticed by Hammarsten. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Effront's Method for the Purification and Preservation of Yeast by means of Hydrofluoric acid or Fluorides. By A. JÖRGENSEN and J. C. HOLM (*Chem. Zeit.*, 17, No. 23).—The authors point out that the principle of this method is the same as that of Pasteur's (Abst., 1892, 904), which consists in treating the yeast with tartaric acid, and that it is inconceivable that a single substance should only act favourably towards the one desired species of yeast and detrimentally towards all the disease germs, and all the undesirable cultivated yeasts which may be present. They show further that the development of a number of known disease germs is actually favoured by this treatment, just as Hansen proved to be the case with the tartaric acid treatment, so that such disease germs may get the upper hand and the desired cultivated yeast become suppressed.

The authors have made an elaborate series of experiments in order to practically test Effront's method, from which the following results may be quoted:—

(1) A distillery yeast, which contained *Mycoderma* in such small amount that it could be detected only with difficulty by the microscope, showed a very strong development of this impurity after treatment by Effront's method. (2) Pure cultures of *Mycoderma* and *Bacterium aceti* were added in very small quantity to a pure culture of a distillery yeast. After treatment with ammonium fluoride, the *Mycoderma* cells were found to have multiplied very freely, whilst

Bacterium aceti was by no means suppressed. In another experiment *Bacterium aceti* was found to have multiplied considerably. In an experiment with a pure brewery yeast (low) to which a very small quantity of *Mycoderma cerevisiæ* was added, the yeast was almost entirely suppressed by the latter organism. (3) A distillery yeast which gives good results in practice was mixed with 20 per cent. of a brewery yeast (low), and after treatment twice by Effront's method, the distillery yeast was *completely crowded out* by the beer yeast. (4) In another mixture of an excellent distillery yeast with a small quantity of a brewery yeast (high), *Sacch. cerevisiæ I*, Hansen, the latter yeast gained the upper hand. (5) In experiments with mixtures of the yeast known as *Carlsberg II* with small quantities of *Sacch. Pastorianus III*, Hansen, the latter, which is a disease yeast, multiplied considerably, and in one case the yeast *Carlsberg II* almost completely disappeared. Similar results were obtained with mixtures of a distillery yeast with small quantities of *Sacch. Pastorianus III*.

The above results show that treatment by Effront's method favours the development of the so-called *disease yeasts*, of *Mycoderma*, of brewery yeasts when present in distillery yeasts, and finally also of *Bacterium aceti*, and the conclusion cannot be too strongly emphasised, that the employment in practice of hydrofluoric acid and the fluorides for the purification and preservation of yeast is attended with very great danger.

A. K. M.

Alcoholic Fermentation of Jerusalem Artichokes under the Influence of Pure Yeast. By L. LÉVY (*Compt. rend.*, 116, 1381—1382).—An extract of Jerusalem artichokes in water containing 0.2 per cent. of potassium hydrogen tartrate was sterilised, and then mixed with pure yeast from Romane Conti, or with a ferment resulting from a cultivation of this yeast on an infusion of barley. Fermentation takes place rapidly at 20—25°, and is complete in about three days. The chief product is ethyl alcohol of good flavour, together with a comparatively small quantity of aldehyde and a still smaller quantity of higher alcohols. In the quality of the main product and the low proportion of the head and tail products, fermentation with pure yeast has a considerable advantage over the ordinary method.

C. H. B.

Assimilation of Atmospheric Nitrogen by Microbes. By S. WINOGRADSKY (*Compt. rend.*, 116, 1385—1388).—It is an established fact that elementary nitrogen is fixed by leguminous plants in symbiosis with microbes, and by mixtures of the lower organisms inhabiting soils, green algæ, and microbes. But the power of nitrogen fixation cannot as yet be ascribed to any particular kind. In the experiments now described, cultivations of soil organisms were made in nutritive solutions (prepared with distilled water, specially purified salts, and very pure dextrose), in closed vessels, the air of which was purified by means of potash and sulphuric acid. In each experiment, gas was liberated, and an acid (chiefly butyric) formed, and finally masses of matter were seen, formed by a large bacillus, and frequently containing spores. These bacilli were conspicuous by their normal appear-

ance and the relative richness of their development. The bacillus could not be obtained in a state of perfect purity, but the two others which remained with them were quite insignificant, and seem to be of no importance as far as the present investigation is concerned, inasmuch as they only develop in the presence of combined nitrogen.

The large bacillus resembles Fitz's *B. butylicus* in many respects, but cannot yet be stated to be identical.

The following figures show (1) the weight of dextrose employed (in grams) in the experiments, (2) the weight of nitrogen given (if any), and (3) the amount of free nitrogen fixed (in milligrams).

Experiment:	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Dextrose.	1	1	1.5	6	3	?	1	1	3	6	7
N ₂ added.	—	—	—	—	—	—	—	2.1	—	—	—
N ₂ fixed..	3.0	2.3	4.5	10.4	8.9	7.2	2.7	2.4	8.1	12.8	14.6

Experiment:	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.
Dextrose....	4	?	4	5	2	2	2	2	2	2
N ₂ added....	2.1	2.1	2.1	3.0	—	—	—	1.8	4.0	3.3
N ₂ fixed	8.4	5.6	14.3	12.5	3.1	2.9	2.5	1.7	0.6	0.8

The question arises whether there is any relation between the amount of sugar decomposed and the nitrogen fixed, whether assimilation can take place at the expense of organic matter other than sugar, such as the organic matter of soils, and what are the most favourable conditions for nitrogen fixation.

N. H. M.

Assimilation of Carbonic Anhydride by Chlorophyllous Plants. By A. BACH (*Compt. rend.*, 116, 1145—1148).—Sulphurous acid, when exposed to sunlight, decomposes with formation of sulphuric acid, water, and sulphur. In a similar manner, carbonic acid (H₂CO₃) might be supposed to decompose with formation of a compound, H₂CO₄ (which would be the acid corresponding with Berthelot's anhydride, CO₃) and formaldehyde [H₂O + C]. The acid, as soon as formed, would decompose, yielding carbonic anhydride and hydrogen peroxide; the presence of the latter in plants was observed by Wurster (*Abstr.*, 1887, 295; compare also Bokorny, *Abstr.*, 1888, 751).

The following experiments were made, the results of which, if not conclusive, are, at least, in accordance with the author's theory:—

A stream of pure carbonic anhydride was passed through two flasks, each containing a 1.5 per cent. solution of uranium acetate. One flask was exposed to direct sunlight; the other was covered with black paper to exclude light. Some more of the solution was exposed to sunlight in a closed flask. The contents of the flask containing the solution treated with carbonic anhydride and exposed to sunlight became turbid and more or less greenish in about 20 minutes; after some time, there was a considerable deposit, which, when filtered and washed, had a violet colour. This precipitate, when exposed, became yellow, and was transformed into a mixture of uranous and uranic hydroxides, with a trace of a brownish substance, probably uranium peroxide. The solutions exposed to the action of sunlight alone and of carbonic anhydride

alone remained unchanged. The reaction is explained thus: The carbonic acid would be converted into aldehyde and percarbonic acid, which would form uranium percarbonate: this would decompose into uranium peroxide and carbonic anhydride. The reduction of uranium peroxide to uranic and uranous hydroxides might be brought about by the aldehyde. A separate experiment was made, in which uranium peroxide was exposed to the action of hydrogen peroxide and formaldehyde; the yellowish precipitate acquired a greenish colour, and was finally transformed into the violet-brown substance soluble in acetic acid.

N. H. M.

Condensation of Carbonic Anhydride under the Influence of Sunlight. By A. BACH (*Compt. rend.*, 116, 1389; compare preceding abstract).—Solutions of dimethylaniline dissolved in water (20 parts), to which sulphuric acid (1 part) had been added, were exposed to sunlight under the following conditions:—No. 1, in an open flask. No. 2 was exposed in a flask through which carbonic anhydride was being passed. No. 3, like No. 2, but wrapped round with grey filter paper. After a lapse of two hours, 30 c.c. of solution was removed from each flask for examination, when it was found that in the case of No. 1 no effect had been produced; in No. 2 tetramethyldiamidophenylmethane was produced in an amount sufficient to give a very intense reaction; in No. 3 a trace of this compound was found. The result shows that the carbonic anhydride had been converted by the action of sunlight into aldehyde, which reacted with dimethylaniline, yielding the above tetramethyl compound. The reaction is of extreme delicacy, and is shown in all degrees of intensity according to the amount of light employed. An ordinary gas flame is sufficient.

N. H. M.

Iron in Plants. By A. MOLISCH (*Bied. Centr.*, 22, 336—338; from *Bot. Centr.*, 50, 370).—Iron occurs in plants partly in a loose form (when it may be extracted by means of acid) and partly in closer union with the plant, so that it can only be detected in the ash. Algæ and fungi seldom contain any considerable amount of iron which may be directly extracted with acid, but large quantities are found in certain lichens. Some mosses (*Fontinalis* and *Miliachoferia*) are rich in iron. The deposits occur chiefly in the membrane, and sometimes impart a brownish colour to the older leaves. Iron is, however, not necessary for the growth of these mosses. A remarkable case of iron accumulation is the fruit shell of *Trapa natans*, the ash of which contains 68 per cent. of ferric oxide.

Insoluble iron is of very general occurrence in plants. As regards iron bacteria, the author does not attach the same importance to iron as Winogradsky, but considers it to be unnecessary for the bacteria, and of no more importance than the deposition of silica in grasses. In the examination of 34 samples of bog iron ore from various mines, there were only two cases where considerable quantities of iron bacteria were found, a result not in favour of Winogradsky's assumption that these ores were produced by the bacteria.

Carefully executed investigations on chlorophyll furnished results which indicated that chlorophyll does not contain iron. Chlorose

occurs as a symptom of a disease produced by abnormal nutrition. Iron is as necessary for fungi as for green plants. Results contrary to this were due to the fact that the nutritive solutions employed were never quite free from iron, and that fungi are able to appropriate the smallest amounts of it.

N. H. M.

Migration of the Starch of Potatoes in the Tubers. By A. GIRARD (*Compt. rend.*, 116, 1148—1151).—Prunet has already showed that the parts of sprouted tubers where the young shoots start are especially rich in starch, and that there may be a difference of as much as 4·2 per cent. in the amount of starch of sprouted and non-sprouted tubers. He concluded that during germination the nutritive matters migrate to the parts where new life is manifested. A similar migration produced by the dry weather of 1892, but much more extensive, was observed in the study of seed potatoes. The drought lasted until July (when the tubers form), and, with slight interruptions, into the middle of August. Regularly formed tubers were produced, but weighing only 50 to 60 grams. The abundant rain of the next two months caused the tubers to develop suddenly; at the top of each, the terminal bud gave rise to an often enormous shoot (increasing the weight to as much as 300 or 400 grams). On separating some of these hour-glass shaped tubers into two parts and determining the starch in both parts, a difference of as much as 12—13 per cent. was found; the original tubers played the part of seed potatoes, and gave up the greater part of their starch to the newly developed portions. This migration of starch was fully confirmed by the microscopical examination of the different parts of the tubers. Taking a section of the tubers, it was found that near the umbilicus the cells were free from starch, at half the length some grains of starch were found, whilst at the top the cells abounded in starch. Moreover, a zone was found in which the few remaining grains were undergoing solution previous to their departure.

N. H. M.

Occurrence of Betaine and Choline in Wormseed (*Artemisia Gallica*, Wild.). By E. JAHNS (*Ber.*, 26, 1493—1496).—The finely-divided seeds are extracted with hot water, the solution treated with lead acetate and soda and subsequently with chloroform; the bases are then precipitated from the aqueous solution with potassium bismuthiodide in presence of sulphuric acid, the precipitate is digested with recently prepared silver carbonate and water, and the compounds are separated by means of absolute alcohol, in which, at ordinary temperatures, choline hydrochloride is readily soluble, whilst betaine hydrochloride scarcely dissolves.

The bases were identified by their own properties and by those of their aurochlorides and platinochlorides.

Betaine platinochloride is deposited in anhydrous needles and also in tabular crystals containing $3\text{H}_2\text{O}$, instead of 4 mols. as stated by Liebreich. The seeds contained about 0·5 per cent. of betaine and 0·1 per cent. of choline.

J. B. T.

Soil and Nitrification. By P. P. DEHÉRAIN (*Compt. rend.*, 116, 1091—1097).—Drainage from unmanured land, and land which was manured with 60,000 kilos. of farmyard manure per hectare, contained the following amounts of nitric nitrogen (kilos. per hectare):—

	Spring.	Summer.	Autumn.	Winter.
Unmanured	28·87	15·21	31·69	15·17
Manured	52·21	24·79	42·89	19·44

In practical agriculture, only a portion of this nitrogen is utilised; wheat and oats take up the nitrates formed in the spring, root crops that formed in the summer; the nitrates formed in the autumn and winter are lost.

In 1891, large vessels were filled with soil from Vauteuil (Seine-et-Marne), and the drainage from the soils collected and examined. The following amounts of nitric nitrogen were obtained per cubic metre of soil.

	No. 1.	No. 2.
24th March, 1891	584 grams	539 grams.
7th April, „	664 „	466 „

Other soils examined in 1892 gave 884 grams and 440 grams of nitric nitrogen per cubic metre in July, and 250 and 285 grams six weeks later. It was found that soils give much greater amounts of nitrates when fresh than when kept for some time; thus soil from Wardrecques gave 116 grams of nitric nitrogen in 1890, and only 33 grams in 1891; whilst soil from Blaringhem gave 108 (in 1890) and 39 grams (in 1891). The effect of stirring on the production of nitrates was next studied. Whilst 100 grams of soil which was not touched gave only 2 milligrams of nitric nitrogen, similar soil kept stirred for the same time (1st November to 15th December) gave amounts varying from 39 to 71 milligrams. The soils yielded drainage in February and March which contained per cubic metre of drainage water the following amounts of nitric nitrogen:—

Soil not stirred	18·8 grams.
Soil stirred	1340·0 „

Nitrification was thus enormously increased by stirring the soil. In order to ascertain whether the time of the year had any effect on the energy of the nitrification, fresh samples of soil were taken in different months. Soils taken in November nitrified with great energy, whilst samples of the same soil taken in January and March, and kept at a very favourable temperature, gave at the most only half as much nitric acid as the samples taken in November. The energy of the nitrifying organisms thus varies with the season.

A hectare of soil 0·09 metre deep would weigh about 1000 tons or 10,000,000 times 100 grams. Calculating the results obtained with 100 grams to a hectare of soil, the amounts of nitric nitrogen would be 440 and 710 kilos. respectively, or from four to six times as much as is required in practice.

After discussing the usual method of working the soil, the author

expresses the opinion that, with more suitable implements for the trituration of the soil, a more vigorous nitrification could be induced, analogous to that obtained in the laboratory. N. H. M.

Analytical Chemistry.

Distillation Apparatus for Analysis. By M. MÜLLER (*Zeit. angew. Chem.*, 1893, 229—230).—When estimating nitrogen by the Kjeldahl process, it is of great importance that no fixed alkali shall find its way into the distillate. The author agrees that the apparatus now in use are trustworthy enough when the distillation proceeds quietly, but considers that when the liquid boils briskly, a source of error through spirting may be introduced.

The author connects the distilling flask, which is fitted with a doubly perforated india-rubber cork, with a pipette-like apparatus, one end of which is suitably bent and connected with the condenser. The lower end is bent twice at right angles, and connected by means of an india-rubber joint with a narrow tube which reaches nearly to the bottom of the distilling flask. At a short distance from the bottom of the 70 c.c. pipette is fixed a rectangular wide tube, which just reaches down to the top of the distilling flask and admits the ammoniacal steam. A portion of the steam keeps on condensing in the pipette, and runs back into the distilling flask, carrying with it any trace of fixed alkali which has spirted over. L. DE K.

Estimation of Small Quantities of Combustible Gas mixed with Air. By H. LE CHATELIER (*Ann. Chim. Phys.* [6], 29, 289—320).—In order to assure safety in coal mines, the “fire damp” must be diluted with air by means of efficient ventilation. The air leaving the mine ought not to contain more than 0.5 per cent. by volume of “fire damp.” In order to regulate this ventilation, it is necessary to know the quantity of fire damp which is evolved in a given time; and to arrive at this, the volume of the air circulating within the mine and the percentage of “fire damp” which it contains must be ascertained. The first of these determinations needs no remarks. To accomplish the second, the author describes the following method, which occupies the first section of the paper. Pure air may be rendered inflammable by adding to it 6 per cent. by volume of methane, but obviously it will be necessary to add a less quantity of methane in order to render air inflammable which already contains “fire damp.” The principle of this method has already been made use of by Schaw, but he did not succeed in solving the practical difficulties of the problem. The author has obtained estimations which are accurate to 0.1 per cent. He employs a graduated glass eprouvette of special construction, in which the combustible mixture is prepared.

In the second section of the paper, another method of estimating

the percentage of combustible gas mixed with air is described, which depends on the combustion of the mixture in contact with incandescent wires. A. R. L.

Volumetric Estimation of Free Chlorine. By C. FRIEDHEIM (*Zeit. anorg. Chem.*, **4**, 145—150).—It is well known that when this estimation is carried out by adding chlorine water to sodium carbonate solution, then adding potassium iodide, and titrating the liberated iodine with thiosulphate, the obtained results are too low. This is not through the formation of iodite or iodate, because, although more iodine may be liberated by acidifying the mixture after finishing the first titration, the total amount liberated is still less than is equivalent to the chlorine taken. Accurate results are, however, obtained if the chlorine is absorbed in sodium carbonate, the solution added to another of potassium iodide containing excess of sulphuric acid, and the liberated iodine then titrated. The real reason of the discrepancy above noticed is that, in alkaline solution, the thiosulphate is in part oxidised to sulphate, instead of exclusively to tetrathionate.

C. F. B.

Specific Gravity of Solutions of Bleaching Powder. By G. LUNGE and F. BACHOFEN (*Zeit. angew. Chem.*, 1893, 326—328).—The authors have constructed a useful table giving the amount of available chlorine corresponding with the specific gravity of solutions of bleaching powder. The specific gravity was taken by means of a delicate hydrometer, showing a difference of 0.0005 at a temperature of 15°. The chlorine was then at once estimated by Penot's arsenic method, which was checked by Lunge's hydrogen peroxide process. When the amount of chlorine is large, the specific gravity process may be taken to be accurate within 0.05 gram of chlorine per litre; when small, within 0.02 gram. L. DE K.

Estimation of Iodine in Haloïd Salts by the Action of Arsenic acid. By F. A. GOOCH and P. E. BROWNING (*Zeit. anorg. Chem.*, **4**, 178—185).—The authors draw attention to the similarity between the method recently published by Friedheim and Meyer (this vol., ii, 183) and that originated by themselves (*Abstr.*, 1890, 1186). They point out that Friedheim and Meyer ought to have obtained better results than they have published; the purity of their reagents is suspected, and doubt is cast on the retention of bromine and chlorine in the retort while distilling over the iodine, if these exceed the limits first laid down by the authors. A. G. B.

Estimation of Fluorine in Combustible Gases. By M. MESLANS (*Bull. Soc. Chim.* [3], **9**, 109—111).—A measured volume of the gas, usually an organic fluoride, is passed into the centre of a glass flask of some 500 c.c. capacity through a glass tube terminating in a platinum one, beneath which a platinum spiral, heated by an electric current, is arranged. The flask contains a known volume of standard potash, and has been previously filled with oxygen under slightly diminished pressure. The gas burns on meeting the incandescent spiral, and the fluorine contained in it forms hydrogen fluoride,

which is at once absorbed by the potash solution; the excess of the latter is determined by titration, or lime water may be used instead of potash, and the resulting calcium fluoride weighed. C. F. B.

Estimation of Phosphorus in Soils. By A. CARNOT (*Bull. Soc. Chim.* [3], 9, 343—346).—10 grams of sifted soil, dried at 100° , is charred if much organic matter be present, moistened first with water and then with nitric acid until there is no more effervescence, and finally digested with 10 c.c. of nitric acid for two hours at about 100° with frequent stirring and addition of fresh acid to replace that which has been evaporated. The mass is washed on to a filter with hot water, the filtrate evaporated to a volume of 50 c.c., and 5 c.c. of concentrated nitric acid, together with 0.5 gram of chromic acid crystals, are added; the dish is then covered with a clock glass, and its contents heated to boiling for half an hour. 5 grams of ammonium nitrate and 50 c.c. of ammonium molybdate solution are next added, and the liquid kept at a temperature of about 100° for an hour, at the end of which time the phosphoric acid will have been completely precipitated. The ammonium molybdate solution is prepared by dissolving 150 grams of the crystallised salt in a litre of water, and pouring the solution into a litre of nitric acid of sp. gr. 1.20; after the liquid has been kept at 60° for three or four days, it is decanted from the deposit. The precipitate is washed by decantation twice with water containing one-fifth of its volume of ammonium molybdate solution, the washings being passed through a small filter, and dissolved in 30 c.c. of ammonia diluted with an equal bulk of warm water. The solution, which, together with the washings, measures 80 c.c., is now neutralised with nitric acid, care being taken that the temperature does not rise above 40° . When the yellow precipitate ceases to redissolve on agitating the liquid, a mixture of 3 c.c. of pure nitric acid, 4 or 5 c.c. of water, and the same quantity of molybdate solution is added. After the precipitate has settled for two hours, it is filtered through a weighed filter, washed first with water containing 1 per cent. of nitric acid and finally with a little pure water, dried at 100° , and weighed. The weight of the precipitate multiplied by the factor 0.0373 gives the quantity of phosphoric acid contained in the 10 grams of soil.

The author has convinced himself that the second precipitation of the yellow precipitate renders unnecessary the tedious process, generally adopted, of rendering the silica of the soil insoluble; the introduction of sodium silicate into the solution did not appreciably alter the percentage of phosphoric acid found. A. G. B.

Estimation of Phosphoric acid as Magnesium Pyrophosphate. By H. NEUBAUER (*Zeit. anorg. Chem.*, 4, 251—266; compare this vol., ii, 236).—Ammonium magnesium phosphate varies in composition with the conditions under which it is precipitated, and three cases may be recognised:—(1) When the precipitate is formed in a neutral or ammoniacal solution, which does not contain an excess of magnesium salt. In this case the ammonium salts present so affect the precipitate that it contains less magnesia than is required for the

normal salt; this entails a loss of phosphoric acid when the precipitate is ignited. (2) When the precipitate is thrown down by the addition of an excess of magnesium salt, no excess of ammonia being present. In this case, normal ammonium magnesium phosphate is produced, and the analytical results are correct. (3) When the precipitate is thrown down by an excess of magnesium salt in the presence of an excess of ammonia. In this case the precipitate contains more magnesia than is required for the normal salt, and the analytical results are too high.

The author recommends the following method:—The separation of the ammonium phosphomolybdate is effected as usual, care being taken that precipitation of free molybdic acid is avoided. The precipitate is dissolved in 100 c.c. of cold $2\frac{1}{2}$ per cent. ammonia solution, and the phosphoric acid precipitated by dropping in, with constant stirring, as many c.c. of magnesia mixture (55 grams of crystallised magnesium chloride and 70 grams of ammonium chloride dissolved in 1 litre of $2\frac{1}{2}$ per cent. ammonia solution) as there are centigrams of phosphoric anhydride present. At least one minute should be occupied in adding 10 c.c. of the magnesia mixture. After the precipitation, the liquid is vigorously stirred, and left for at least three hours, when the precipitate is collected and washed with $2\frac{1}{2}$ per cent. ammonia water until the chlorine reaction has disappeared. The dried filter is transferred, with the precipitate, to a platinum crucible, and burnt, the temperature being gradually raised to a medium red heat until the precipitate is quite white. Ignition over the blowpipe until the weight is constant is necessary. To the weight of the magnesium pyrophosphate must be added a correction for the loss on ignition; a table is given which shows the milligrams to be added to quantities of pyrophosphate from 0.01 to 0.35 gram; in the last case, the correction amounts to 11 milligrams.

A. G. B.

Volumetric Estimation of Phosphoric acid. By A. F. HOLLEMAN (*Rec. Trav. Chim.*, 12, 1—11).—Various volumetric methods hitherto employed are enumerated, discussed, and rejected as unsatisfactory. The following method is then proposed:—In a flask of 200 c.c. capacity are placed 50 c.c. of the liquid to be analysed (which should not contain more than 0.2 gram of phosphoric acid), 10 c.c. of a normal solution of sodium acetate, and then a slight excess of decinormal silver nitrate (4.5 c.c. for every 0.01 gram P_2O_5 supposed to be present). The solution is then neutralised with N/10 soda, the amount required having been determined by previously titrating 10 c.c. of the liquid to be analysed, using phenolphthaleïn as indicator; five times this amount is, of course, taken, or, better, five times less $\frac{1}{2}$ c.c. The phosphoric acid is, in the presence of sodium acetate, completely precipitated as silver phosphate, and the excess of silver is determined by diluting the mixture to 200 c.c., filtering, and titrating 100 c.c. of the filtrate with thiocyanate according to Volhard's method. The results agree well with those obtained gravimetrically. Sulphuric and nitric acids may be present, but not hydrochloric. Alkali and alkaline-earth metals may be present, but not heavy metals. If iron and aluminium are present, 100 c.c. is

precipitated with 20 c.c. of normal sodium acetate, the phosphoric acid is determined in 50 c.c. of the filtrate, and the precipitate of iron and aluminium phosphates is ignited and weighed, and its weight, multiplied by 0.45/2, is added to the weight of phosphoric anhydride found volumetrically. If ammonia is present, it must be removed by boiling with soda, as, otherwise it affects the titration with phenolphthaleïn.

C. F. B.

Estimation of Boric acid. By A. K. REISCHLE (*Zeit., anorg. Chem.*, **4**, 111—116).—Several of the methods hitherto used have been examined and found defective; the following is recommended. The substance is slowly warmed in a platinum crucible with six times its weight of resublimed ammonium fluoride, when ammonium borofluoride volatilises. After cooling, the residue is treated with strong sulphuric acid, evaporated to dryness, and ignited. From the difference in weight of the sulphate found and borate taken, the amount of boric acid originally present may be calculated. The results are accurate; with borax they varied from 99.6 to 99.9 (in one case 99.3) per cent. of the theoretical; in the case of a mixture of freshly-ignited lime with boric acid, from 100.3 to 100.5 (in one case 98.5) per cent.

C. F. B.

Analysis of Silicates by Deville's Method. By F. GLINKA (*J. Russ. Chem. Soc.*, **24**, 456—458).—The author uses Deville's method of silicate analysis in preference to those usually employed, as it admits of the determination of silica, alumina, and alkalis in one portion of material; he considers it specially applicable to soda felspars. A weighed quantity of powdered albite is mixed with the same weight of pure powdered calcium carbonate in a small platinum crucible, which is carefully heated first over a MÜNCKE burner, and finally over the blowpipe, the heat being very gradually applied, until at last the whole mass has fused to a homogeneous liquid, which is kept fused for 10—15 minutes. On cooling, the melt can be easily decomposed by means of nitric or hydrochloric acid. The analysis is then conducted in the ordinary manner.

The calcium carbonate employed was prepared by dissolving marble in nitric acid, evaporating to drive off the acid, dissolving in water, and precipitating with ammonium carbonate. The filtered and carefully-washed precipitate was dried first at the ordinary temperature, and finally at 130—150°.

J. W.

Estimation of Carbon in Iron and Steel. By O. PETTERSSON and A. SMETT (*Zeit. anorg. Chem.*, **4**, 305—308).—This method has already been described (*Abstr.*, 1890, 1027); it is now proposed to absorb the sulphurous anhydride by solid chromic acid, and to pass the gas over red-hot copper oxide before it is absorbed by the baryta water, in order to burn any hydrocarbons. A convenient form of apparatus is figured.

A. G. B.

Estimation of Carbon in Steel. By R. LORENZ (*Zeit. angew. Chem.*, 1893, 313—324, 395—397, 411—414).—The author criticises the various processes in use for the estimation of carbon in steel,

and comes to the conclusion that when accurate results are wanted, the carbon should be estimated by direct combustion.

This process is not new, having been, in fact, employed and recommended by Regnault. But, after investigation by many eminent chemists, it has been practically abandoned, as the results obtained were generally below the truth.

The author has now revived the process. The finely divided sample is mixed in a porcelain boat with fused and powdered lead chromate. The boat is placed inside a long porcelain tube, which is now put in a specially constructed furnace, previously described by the author, a modification of the well-known Glaser furnace, by means of which a powerful white heat can be obtained.

The sample is burnt in a current of pure and dry oxygen, which then passes over red-hot copper oxide, contained in a second porcelain boat, heated in an ordinary gas combustion furnace. The carbonic anhydride formed by the combustion of the steel is passed through a series of soda-lime absorption tubes, and finally weighed.

L. DE K.

Volumetric Estimation of Copper, Iron, and Antimony, and of Zinc in Zinc Powder. By F. JEAN (*Bull. Soc. Chim.* [3], 256—258).—The method described for the estimation of copper is that devised by Weil in 1869, which consists in titrating a boiling solution of cupric salt, in the presence of a large excess of hydrochloric acid, with stannous chloride. Stannous chloride (4.5–5 grams) is dissolved in water (100 grams), and hydrochloric acid (30 grams) added. The titration is conducted in a flask of white glass, in the presence of 0.25 gram of hydrochloric acid; the stannous chloride is added drop by drop to the boiling solution until the colour is quite destroyed. Ferric chloride may be titrated in like manner. To estimate iron and copper in the presence of each other, the volume of stannous chloride solution necessary for the reduction of the two salts is first ascertained, the copper is then precipitated by boiling the solution with granulated zinc, and the iron titrated alone. Antimony perchloride may also be titrated with stannous chloride. To estimate antimony and copper in a solution containing both metals, the two are first titrated together, the copper is then reoxidised by a current of air or by potassium permanganate, and the solution again titrated.

When zinc powder is treated with an excess of a neutral solution of copper of known titre, an equivalent amount of copper is precipitated, and by titrating the excess with stannous chloride solution, the percentage of zinc may be estimated. Test analyses are not given.

A. R. L.

Separation of Metals in Alkaline Solution by Hydrogen Peroxide. By P. JANNASCH (*Ber.*, 26, 1496—1499; compare Abstr., 1892, 537).—*Separation of Lead from Silver.*—About 0.5 gram of each of the nitrates is dissolved in water (50 c.c.), the solution acidified with concentrated nitric acid (2 c.c.), and treated at ordinary temperatures with a mixture consisting of 15—20 c.c. of hydrogen peroxide (2 per cent.) and 15 c.c. of concentrated ammonia; saturated solution

of ammonium carbonate (5 c.c.) is then added, the brownish-yellow lead oxide is separated, washed with dilute ammonia, then with water, and ignited in a platinum crucible which is placed in an air-bath, the residue is treated with nitric acid, the nitrate dissolved in water, the solution evaporated to dryness, and the residue weighed after fusion.

The filtrate containing the silver is evaporated until free from ammonia, acidified with nitric acid, and the silver determined in the usual manner.

The lead may also be precipitated with hydrogen peroxide, in presence of ammonium sulphate, in sulphuric acid solution, but greater attention requires to be paid to the strength of the various reagents.

Separation of Silver from Bismuth.—This is effected in a similar manner to the preceding; the addition of ammonium carbonate is unnecessary.

The numerical results show that a considerable degree of accuracy can be attained by this method of separation. J. B. T.

Separation of Lead from Silver in Ammoniacal Solution by means of Chromic acid. By P. JANNASCH (*Ber.*, 26, 1500; compare preceding abstract).—The mixed nitrates (0.5–0.6 gram of each) are dissolved in water (100 c.c.), dilute nitric acid (2 c.c.) is added, and the liquid boiled in a porcelain dish; boiling 10 per cent. solution of potassium dichromate (6 c.c.) is then added, and afterwards dilute (1:3) ammonia (15 c.c.); the precipitate is heated on the water-bath for 15–20 minutes, allowed to cool, filtered, and washed, first with dilute ammonia, and finally with water. The silver is determined in the filtrate by the ordinary method.

The accuracy of the method is shown by numerical results.

J. B. T.

Analysis of Impure Galena, and a Method of estimating Copper and Zinc. By F. JEAN (*Bull. Soc. Chim.* [3], 9, 253–258).—25–30 grams of the mineral, finely pulverised and passed through a silk sieve, are boiled for an hour in a porcelain capsule with a concentrated solution of sodium sulphide, to which sulphur is added, the water being replaced at intervals as it evaporates. The liquid is now diluted with water, and after a while the clear solution is decanted, and the insoluble matter washed by decantation. The solution is acidified, and the precipitated sulphides of antimony and arsenic collected, dried, and weighed; when their amount is large, an aliquot portion, or when otherwise, the whole, is treated with aqua regia at a moderate temperature, and the solution filtered from sulphur, the latter being again treated with aqua regia. The united liquids are concentrated, boiled, with the addition of hydrochloric acid, until chlorine is no longer evolved, and made up with water to 100 c.c. The antimony is then estimated in 25 c.c. of the solution by titrating it with a standard solution of stannous chloride, in the presence of 10 c.c. of a solution of copper sulphate containing 0.7 gram of that salt (Weil's method). After ascertaining the relative values of the copper and stannous chloride solutions, the amount of copper used in the test is deducted from the amount (calculated as copper)

found in the test; the difference multiplied by 0.66214 gives the antimony. The arsenic is estimated in another 25 c.c. portion of the solution by precipitation as ammoniomagnesian arsenate in the presence of tartaric acid.

The mineral, deprived of antimony and arsenic, is heated to redness, in an iron scorifier, with 10 grams of ammonium nitrate; after three or four such treatments, the sulphides are transformed into oxides. The pulverised mass is then digested with hydrochloric acid, in a porcelain capsule, to dissolve the zinc and copper; a little lead also goes into solution, but the greater portion remains as oxide; the mixture is diluted with water (500 c.c.), and allowed to remain, in order that the lead chloride (and also a little silver chloride) may separate. The clear liquid is decanted, the residue washed by decantation, the whole of the liquors united, and sodium phosphate added, which precipitates the lead chloride, the manganese, magnesium, and calcium; subsequently ammonia and ammonium chloride are added. The precipitate is dried and added to the principal residue containing the remainder of the lead and silver, which is then fused in a crucible with sodium carbonate, a little borax, and 1—2 grams of flour. The metallic button of lead and silver is then weighed, and the silver estimated by cupellation.

The ammoniacal solution contains copper and zinc, the amounts of which are estimated by titration with a solution of sodium sulphide, employing paper impregnated with lead carbonate as indicator. [The titre of the sodium sulphide solution is previously ascertained by direct titration of ammoniacal solutions containing known weights of zinc and copper.] The copper is then, after acidification, precipitated in another portion of the solution as sulphide, and ammonia and ammonium carbonate added to the filtrate, in which the zinc is then estimated alone by titration with sodium sulphide. Test analyses are not given. A. R. L.

Analysis of Pigments ground in Oil. By J. B. HANNAY (*Chem. News*, 67, 268—269).—To completely extract oil from ground pigments, the author recommends using no less than 100 c.c. of fresh methylated ether for every gram of the sample. On treating ground white lead in this manner, he has always succeeded in getting a residue perfectly soluble in dilute nitric acid. The author ridicules the idea that Dutch white lead owes its superior quality to the fact that it causes a saponification of the oil. On passing hydrogen sulphide into the ethereal solution, he has never succeeded in obtaining a precipitate of lead sulphide, showing the absence of lead oleate.

L. DE K.

Analysis of Ground White Lead. By R. H. HARLAND (*Chem. News*, 67, 301).—The author does not agree with Hannay (see preceding abstract), and states that after extracting 50 grams of Stack white lead with 5 litres of ether, the residue did not dissolve to a clear solution in nitric acid, but a distinct trace of oil separated. The ethereal solution, after its volume had been greatly reduced by distillation, gave a distinct black precipitate with hydrogen sulphide.

L. DE K.

Quantitative Analysis by Electrolysis. By A. CLASSEN (*Zeit. anorg. Chem.*, **3**, 404—406).—A further reply to Rüdorff (this vol., ii, 391).

Electrolytic Separation of Metals. By E. F. SMITH and J. C. SALTAR (*Zeit. anorg. Chem.*, **3**, 415—420).—*Copper from Bismuth.*—The text-books are not agreed as to the possibility of this separation in the presence of free nitric acid. The authors find that either metal alone can be completely precipitated, provided, in the case of bismuth, that the amount of nitric acid is not more than is necessary to prevent the formation of basic nitrate, otherwise part of the bismuth is deposited on the anode as peroxide. But from a solution containing both metals, the copper, although completely precipitated, is always contaminated with bismuth, and a further portion of the latter is precipitated as peroxide on the anode.

Lead from Bismuth.—Lead is completely precipitated as peroxide from a solution containing free nitric acid, but in the presence of bismuth the peroxide is invariably contaminated with that substance.

Copper from Lead and Bismuth.—Copper can be completely precipitated in a pure condition from solutions containing free nitric acid and small quantities (up to 1 per cent. of the copper) of lead and bismuth, but when larger quantities are present, the metal is contaminated, both with lead peroxide and with metallic bismuth.

JN. W.

Separation of Copper from Bismuth. By A. CLASSEN (*Zeit. anorg. Chem.*, **4**, 234—235).—The author disclaims origination of the statement in his book on electrolysis, quoted by Smith and Saltar (preceding abstract). It has long been known that copper cannot be deposited pure when bismuth is present. That bismuth cannot be separated electrolytically from lead in a nitric acid solution, nor mercury from bismuth, under similar conditions, has already been pointed out by the author (*Ber.*, **19**, 323).

A. G. B.

Electrolytic Separation of Copper from Antimony. By E. F. SMITH and D. L. WALLACE (*Zeit. anorg. Chem.*, **4**, 273—274).—If antimony be converted into a higher oxide by bromine, and the solution containing it be mixed with tartaric acid, and made strongly alkaline with ammonia, no antimony will be deposited on electrolysis. This fact is applied to the separation of copper from antimony by electrolysis; the deposition of the former metal being complete under the above conditions.

A. G. B.

Volumetric Estimation of Mercury. By J. LABORDE (*J. Pharm.* [5], **27**, 507—509).—This new method of estimating mercury, present in the mercuric state, depends on the fact that when a solution of stannous chloride is added to a solution of a mercuric salt, the pure white colour of the mixture, due to precipitated mercurous chloride, changes to brown as soon as enough stannous chloride has been added to reduce all the mercuric to mercurous salt, a further reduction to metallic mercury then beginning. The solution is made by dissolving 8 grams of tin-foil in 100 c.c. of hydrochloric acid, and

diluting; it is standardised against a solution containing 10 grams of pure mercuric chloride per litre, 5 c.c. of a solution containing 100 grams each of ammonium acetate and acetic acid per litre being added for every 10 c.c. of the mercuric solution. In an actual estimation, free mineral acids must, if present, be neutralised with ammonia, ammonium acetate being first added. The reaction is affected only by the presence of gold or platinum salts, or of iron salts in large quantity. The method is rapid and accurate, and can be carried out in very dilute solution; it may also be used in the reverse sense to estimate stannous chloride.

C. F. B.

Electrolytical Separation of Mercury from Bismuth. By E. F. SMITH and J. B. MOYER (*Zeit. anorg. Chem.*, **4**, 96—99).—It is not the case, as is implied in Classen's *Quantitative Analyse durch Electrolyse*, 3rd ed., p. 147, that mercury can be separated from bismuth by electrolysis in a solution containing free nitric acid. The mercury is, it is true, completely precipitated, except when the current is small and the amount of acid large, but it is always contaminated with bismuth, as, indeed, Classen has himself stated (*Ber.*, **19**, 325), and some bismuth is also deposited on the anode.

C. F. B.

Electrolytic Separations. By E. F. SMITH and J. B. MOYER (*Zeit. anorg. Chem.*, **4**, 267—272; compare Smith and Saltar, *J. Anal. Chem.* **7**, 128).—*Mercury from Lead.*—Mercury, as mercuric nitrate, 0.1150 gram; lead, as nitrate, equivalent to 0.0126 gram of lead peroxide; nitric acid (sp. gr. 1.3), 30 c.c.; total volume, 175 c.c.; current, 1.8 c.c. detonating gas per minute. Mercury deposited, 0.1150 gram; lead peroxide deposited, 0.0126 gram.

Silver from Lead.—Silver, as nitrate, 0.1208 gram; lead, as nitrate, equivalent to 0.0144 gram of lead peroxide; nitric acid (sp. gr. 1.3), 15 c.c.; total volume, 200 c.c.; current, 1.8 c.c. detonating gas per minute; silver deposited, (1) 0.1023, (2) 0.1028 gram; lead peroxide deposited, (1) 0.0144, (2) 0.0145 gram.

Copper from Cadmium.—Copper, as sulphate, 0.1341 gram; cadmium, as nitrate, 0.1 gram; nitric acid (sp. gr. 1.2), 5 c.c.; total volume, 200 c.c.; current, 0.6 c.c. detonating gas per minute. Copper obtained, 0.1346 gram, containing no cadmium.

Copper from Zinc.—Metals, the same weight as for copper from cadmium; nitric acid (sp. gr. 1.3), 5 c.c.; total volume, 200 c.c.; current, 1 c.c. detonating gas per minute; copper deposited, 0.1345.

Copper from Zinc, Cobalt, and Nickel.—Metals, the same weights; nitric acid (sp. gr. 1.3), 5 c.c.; total volume, 200 c.c.; current, 0.4 c.c. detonating gas per minute. Copper deposited, 0.1339 gram.

Copper from Iron and Zinc.—Metals, the same weights; volumes, the same; current, 0.7 c.c.; copper deposited, 0.1340 gram.

Bismuth from Cadmium.—Bismuth, as nitrate, 0.0718 gram; cadmium, as nitrate, 0.1 gram; nitric acid (sp. gr. 1.1), 15 c.c.; total volume, 180 c.c.; current, 1.6 c.c.; bismuth deposited, 0.0716 gram.

Bismuth from Nickel.—Bismuth, 0.0718 gram; nickel, 0.1 gram;

nitric acid (sp. gr. 1.3), 3 c.c.; total volume, 200 c.c.; current, 0.2 c.c.; bismuth deposited, 0.0716 gram.

Bismuth from Cobalt.—Bismuth, 0.0718 gram; cobalt, 0.1 gram; nitric acid (sp. gr. 1.3), 3 c.c.; current, 0.2 c.c.; bismuth deposited, 0.0714 gram.

Bismuth from Cobalt, Nickel, and Zinc.—Bismuth, 0.0718 gram; zinc, 0.1 gram; nickel, 0.1 gram; cobalt, 0.1 gram; nitric acid (sp. gr. 1.3), 8 c.c.; total volume, 200 c.c.; current, 0.4 c.c. Bismuth deposited, 0.0718 gram. The separation is attended with greater difficulty than the separation of bismuth from any one of these three metals.

The authors conclude that nitric acid solutions are not so well adapted as those containing sulphuric acid for the electrolytic separation of bismuth from other metals (compare Abstr., 1886, 923).

A. G. B.

Estimation of Manganese Oxides by means of Hydrogen Peroxide. By A. CARNOT (*Compt. rend.*, 116, 1295—1297).—When an oxide of manganese is mixed with hydrogen peroxide in presence of an acid, the volume of oxygen given off is double that of the oxygen present in the oxide over and above that required to form manganous oxide. The oxide is placed in a flask fitted with a cork, which carries a delivery tube and a funnel with a stop-cock. Dilute nitric acid (2:3) is then added, and, after evolution of carbonic anhydride has ceased, the stop-cock is closed. A measured volume of hydrogen peroxide solution is then poured into the funnel, and is allowed to run gradually into the flask, the oxygen evolved being collected over water. If the temperature and pressure remain constant during the experiment, the volume of gas collected, less the volume of the hydrogen peroxide solution added, is the volume of the oxygen.

C. H. B.

Estimation of Manganese by Oxydometric Methods. By A. CARNOT (*Compt. rend.*, 116, 1375—1378).—The estimation of manganese by oxydometric methods requires that the metal shall be in a definite state of oxidation. The ordinary methods of heating the oxide or the nitrate do not give trustworthy results. If, however, the manganese is dissolved in concentrated nitric acid and potassium chlorate is added in successive small quantities to the warm liquid, manganese peroxide is precipitated, and the other metals, as a rule, remain in solution. The whole of the iron is not eliminated at the first, but a repetition of the treatment (the manganese peroxide being first dissolved in a mixture of nitric acid and hydrogen peroxide) yields a pure product.

Even better results are obtained by mixing the manganese solution with hydrogen peroxide, and then quickly adding excess of ammonia and boiling the liquid for some minutes. The product has the composition Mn_6O_{11} or $MnO, 5MnO_2$. Large quantities of ammonium salts tend to prevent the formation of the peroxide, but their influence can be counteracted by the use of a larger quantity of hydrogen peroxide. Copper, zinc, nickel, and cobalt, if present, are partially precipitated in the form of manganites, but the elimination of these metals is easily secured by repeating the precipitation. With large

quantities of copper, nickel, and zinc, three precipitations usually suffice; with cobalt, five may be necessary. Iron does not affect the results of the analysis, but it may be removed, if desired, by first precipitating with nitric acid and potassium chlorate, dissolving the precipitate in dilute nitric acid and hydrogen peroxide, and then precipitating with hydrogen peroxide and ammonia.

The manganese may also be precipitated by bromine and ammonia in the cold, if care is taken that the bromine remains in contact with the almost neutral manganese solution for some time; but the method is not so convenient as that just described. The precipitate has the composition Mn_2O_{11} , and must be well washed with hot water.

C. H. B.

Estimation of Manganese in Minerals. By F. JEAN (*Bull. Soc. Chim.* [3], 9, 248—252).—Pattinson's method of estimating manganese consists in precipitating the metal as dioxide and titrating the latter with strongly acidified ferrous sulphate, and subsequently with potassium dichromate. The author prefers to employ oxalic acid and potassium permanganate. This method is to be recommended when a series of manganese estimations have to be made, but it has the inconvenience of requiring a large number of solutions, and, on this account, the author prefers the following:—The finely pulverised mineral is decomposed by hydrochloric acid, the solution evaporated to dryness, and the silica collected and weighed. The filtrate is made up with water to a volume of 100—200 c.c. 25—50 c.c. of it is precipitated by sodium carbonate, the precipitate collected, redissolved in 50 c.c. of nitric acid (sp. gr. 1.2), and the solution boiled for a quarter of an hour with potassium chlorate (6—8 grams), whereby the whole of the manganese is precipitated as dioxide. It may be weighed as Mn_3O_4 , or titrated with oxalic acid and potassium permanganate.

The author has obtained good results with Guyard's method, operating in the manner described by Campredon (*Mon. Sci.*, 1892). It is specially applicable in the case of spiegel-eisen, manganese steel, and ferro-manganese. The substance is decomposed by aqua regia, the nitric acid expelled by evaporation, and hydrochloric acid added. The solution is maintained at 80°, and treated with an excess of zinc oxide or calcium carbonate, whereby, after well shaking, the iron is precipitated; it is then made up to about 500 c.c. with hot water, and titrated with potassium permanganate. Test analyses are not given.

A. R. L.

Estimation of Iron and Aluminium in Bone Black. By F. G. WIECHMANN (*Chem. News*, 67, 311—312).—The author has devised the following scheme, which offers all the advantages of the Glaser and the Stutzer methods:—5 grams of the sample is dissolved in 30 c.c. of hydrochloric and 10 c.c. of nitric acid, and made up to 500 c.c. 100 c.c. of the filtrate is put into a 250 c.c. flask, and mixed with 25 c.c. of strong sulphuric acid. After well shaking and cooling, absolute alcohol is added up to the mark. As contraction takes place, it is necessary to add, after some time, a little more alcohol. After 12 hours, the liquid is filtered off, and 100 c.c. is evaporated in a

platinum dish until the spirit is expelled. The remaining solution is washed into a beaker with 50 c.c. of water, heated to boiling and rendered alkaline with ammonia, the excess of which must now be completely expelled by boiling. After washing the precipitate thoroughly with boiling water, the filter containing it is placed in a beaker containing 150 c.c. of molybdic solution at 40°, and then kept for about 12 hours at 65°. The liquid is filtered, and the precipitate well washed with a 10 per cent. solution of ammonium nitrate. The filtrate is rendered alkaline with ammonia and boiled for a few hours, a little ammoniacal water being added from time to time. The precipitate now consists of ferric and aluminic hydroxides, but to free it from traces of molybdic acid, it must, after washing, be redissolved in hydrochloric acid and reprecipitated with ammonia. Finally, the precipitate is ignited and weighed, and reported as mixed iron and aluminium oxides.

L. DE K.

Modification of the Stannous Chloride Method of titrating Iron. By R. W. MAHON (*Amer. Chem. J.*, 15, 360).—To determine the end of the reduction in this process, the author employs a solution containing 0.05 gram of platinum, in the form of platinum chloride, and 34 grams of mercuric chloride per litre as indicator. Stannous chloride in presence of this solution reduces the whole of the ferric salt to the ferrous state, and then precipitates a dark cloud of mercurous chloride mixed with metallic mercury and platinum. The iron solution is made up to about 125 c.c., and contains 20–40 c.c. of hydrochloric acid of sp. gr. 1.20; the liquid is heated almost to the boiling point and titrated, after the addition of 15 c.c. of the indicator solution. 0.2 c.c. must be subtracted for the final reaction. Results excellent.

A. H.

Analysis of Iron and Steel. By J. PARRY and J. J. MORGAN (*Chem. News*, 67, 149–150, 161–162, 175–177, 247–248, 259–261, 295–296, 307–308).—The authors describe the most trustworthy processes in use for the estimation of the minor constituents in iron and steel, such as silicon, phosphorus, total and graphitic carbon, manganese, copper, arsenic, nickel, cobalt, chromium, aluminium; also tungsten, titanium, calcium, magnesium, and iron oxide. As regards the rarer of these substances, the authors remark that, although, no doubt, frequently occurring, they are but rarely recorded in analytical certificates, for the simple reason that they are seldom looked for.

Iron oxide (Fe_3O_4), which is always present in the samples, is best estimated by a process devised by Parry. 10 grams of the sample is dissolved at a gentle heat in 500 c.c. of a mixture of potassium dichromate and sulphuric acid (1 part of acid to 6 parts of saturated dichromate solution). When it is judged that the whole of the iron has dissolved, the solution is allowed to remain until settled, when the supernatant liquid is passed through a filter. The insoluble residue is now washed a few times with water by decantation, and afterwards digested with aqueous potash to remove the silica. The residue is now well washed on the filter, first with the alkali and then

with water, until the alkali has been completely removed. The filter is afterwards strongly ignited, and the residual ferric oxide weighed.

L. DE K.

Separation of Nickel and Cobalt by means of Nitroso- β -naphthol. By G. v. KNORRE (*Zeit. angew. Chem.*, 1893, 264—269).—The author recommends the following process for the assay of commercial nickel:—5 grams of the sample is dissolved in 50 c.c. of nitric acid of sp. gr. 1.2, in a covered beaker. When dissolved, the liquid is put into a porcelain dish, 10 c.c. of sulphuric acid is added, and the whole evaporated until sulphuric acid fumes begin to be evolved; when cold, water is added, and the mixture heated until all the nickel sulphate has dissolved. Any insoluble silicic acid is then collected, and should, after weighing, be tested as to its purity by means of hydrofluoric acid.

The filtrate is mixed with 50—100 c.c. of solution of hydrogen sulphide and warmed to assist the separation of any copper sulphide, which may then be collected, washed with solution of hydrogen sulphide, and converted into oxide by ignition. The filtrate is concentrated and, after cooling, made up to 250 c.c. 100 c.c. is pipetted off and freed from iron by the addition of ammonia. As the iron precipitate always contains nickel, it must be twice redissolved and reprecipitated. In another portion, the joint nickel and cobalt are precipitated by electrolysis. The solution is mixed with 5 grams of sodium sulphate and a large excess of ammonia (sp. gr. 0.91). The author employed 6—8 Meidinger cells, or Gölcher's thermo-column. Sodium sulphate is preferable to ammonium sulphate, as the latter forms a less soluble double compound with the nickel. After weighing, the metal is dissolved in nitric acid, evaporated with sulphuric acid, dissolved in dilute hydrochloric acid, and the cobalt precipitated by the addition of nitroso- β -naphthol. Formerly the author adopted the plan of mixing the dried precipitate with oxalic acid before ignition, as the compound is slightly explosive; but he has found that the conversion of the salt into oxide (Co_3O_4) may be effected, without risk, by introducing the moist filter containing it straight into a platinum crucible, which is then at once heated to redness. Operating in this manner, it is also easier to get rid of the last traces of carbonaceous matter. The test analyses given are highly satisfactory. The process is not only serviceable for the precipitation of cobalt in presence of nickel, but also for the separation of iron from aluminium and phosphoric acid, iron from copper or manganese, &c.

L. DE K.

Quantitative Separations in presence of Hydroxylamine. By P. JANNASCH and J. MAI (*Ber.*, 26, 1786—1787).—The addition of a certain quantity of hydroxylamine to the solution of a salt before precipitating the metal with ammonia has frequently a remarkable influence on the result. In some cases, the properties of the precipitate are considerably altered, in others no precipitate is formed, whilst in others precipitates are obtained which are not produced when ammonia alone is used. An example of the first effect is found in the case of chromium, which is precipitated from solutions of its salts by ammonia in presence of hydroxylamine as a violet-red pre-

cipitate; the latter can be collected and washed with much greater ease than the green precipitate obtained by the use of ammonia alone.

Further investigation of the effect of hydroxylamine in quantitative separations is now in progress.
H. G. C.

Assay of Tin Ore. By T. MOORE (*Chem. News*, 67, 267—268).—Half a gram of the ore mixed with 5 or 6 grams of powdered zinc (prepared by tritulating melted zinc in a hot iron mortar and separating coarser particles by sifting) is placed on, and covered with, a layer of the zinc powder in a porcelain crucible, a piece of charcoal is put on the top, and the covered crucible heated in a muffle until the volatilisation of zinc nearly ceases. When cool, the charcoal is removed, and the crucible and its contents treated with hydrochloric acid. The filtered solution is concentrated, made to contain a quarter of its volume of hydrochloric acid, heated nearly to boiling for 15 minutes with 5 or 6 grams of granulated lead, the solution poured into a measured excess of ferric chloride solution, and the unreduced iron titrated with cuprous chloride, using potassium thiocyanate as an indicator; from the amount of iron reduced the amount of tin is found. The heating with lead reduces stannic to stannous compounds without the production of metallic tin.
D. A. L.

Method for the Simultaneous Estimation of Carbon and Nitrogen in Organic Compounds. By F. KLINGEMANN (*Annalen*, 275, 92—102).—The method is that of Frankland and Armstrong (this Journal, 21, 109). The substance (0.1—0.15 at most) is burnt with copper oxide in a tube which is exhausted before and after the experiment with a Sprengel pump. The total volume of the gaseous products is measured, and subsequently that of the residual gas after the absorption of the carbonic anhydride. One experiment takes about $2\frac{1}{4}$ hours.
A. R. L.

Detection of Adulteration in Wines. By MAROUBY (*Bull. Soc. Chim.* [3], 9, 13—16).—Test papers are prepared by soaking blotting-paper in the necessary reagents and drying. From the appearance of the spots caused by drops of wine on the various papers, it is possible to detect many sophistications, as is evidenced by a table given of the appearances of the centres, intermediate and exterior zones of the spots given by wines to which various foreign substances have been added. Foreign colouring matters generally show their effect more in the central and intermediate portions of the spots, the exterior zone being characteristic of the natural colouring matters of the wine.
W. T.

Estimation of the Dry Residue from Wine. By J. A. MULLER (*Bull. Soc. Chim.* [3], 9, 6—10).—The author describes a method of obtaining the dry residue by evaporation at 100° in a current of dry carbonic anhydride. From a series of experiments, the rates of desiccation for wines containing varying quantities of glycerol are deduced; hence the absolute residue at 100° may be calculated by subtracting from the residue, after 12 hours desiccation, a quantity depending on the percentage of glycerol present and the quantity of

wine taken for evaporation, provided that the residue is not much more than 0.1 gram, and the desiccation is carried on exactly in accordance with the prescribed method.

When the dry residue is obtained by means of the vacuum desiccator, the loss of glycerol at 15° may be neglected, but a correction should be applied for loss near 30°.

W. T.

Identification and Estimation of the Lactoses in different Milks. By G. DENIGÈS (*J. Pharm.* [5], 27, 413—417).—Milk of woman, ass, mare, cow, goat, sheep, or bitch yields in each case the same crystallised lactose when the whey is evaporated. The whey itself possesses the same reducing power as a solution of lactose of the same strength, but not the same rotatory power, except after hydrolysis; it behaves as if it contained, in addition to lactose, a substance which does not reduce Fehling's solution, but which is, in the case of the woman and bitch, dextrorotatory; in the case of the ass and mare, lævorotatory, but in all cases loses its optical activity when hydrolysed with dilute acid at 106—110°.

In the estimation of lactose in milk, it is thus best to make use of the reducing power, rather than the optical activity. In a 100 c.c. flask are placed 10 c.c. of the milk, 2.5 c.c. of a 5 per cent. solution of sodium metaphosphate, and 60—70 c.c. of water; the mixture is shaken, 0.5 c.c. of hydrochloric acid is added, and the whole is made up to 100 c.c., shaken, and filtered. The reducing power of the whey thus obtained is determined by means of Fehling's solution, previously standardised against a solution of pure lactose of known strength.

C. F. B.

Polarimetric Examination of Gums. By GUICHARD (*Bull. Soc. Chim.* [3], 9, 19—20).—The author finds several samples of gums, among a number examined, to be dextrorotatory, notwithstanding the assertion of Béchamp that there are no dextrorotatory gums. Commercial acetic acid dissolves the greater part of the dextrorotatory samples, but simply converts the lævorotatory gums into opaque white substances without change of form. The materials examined consist of mixtures of gums of different rotatory powers.

W. T.

Note.—The author appears to be unacquainted with O'Sullivan's "Researches on Gedda Gums," *Trans.*, 1891, 1029.—[EDITORS.]

Detection of Hydrocyanic acid. By S. LOPES (*J. Pharm.* [5], 27, 550—553; from *Revista d. Cursos d. Faculd. d. Med., Rio de Janeiro*).—Some of the observations in this paper have been recently published by Autenrieth (this vol., ii, 393). It is suggested that mercuric cyanide should be looked for after testing for alkaline cyanides; the liquid is acidified with tartaric acid, ammonium chloride is added in excess, and the mixture is distilled; a double chloride of mercury and ammonium is formed, and hydrogen cyanide distils over with the steam. To test for poisonous cyanides in the presence of non-poisonous ones, such as potassium ferrocyanide, the substance is first heated at 100° with milk of lime, in order to decompose ammonium salts, which, if present, might form volatile ammonium cyanide by

reacting with the ferrocyanide; when all the ammonia has been driven off the solution is filtered, and tested as described by Autenrieth.

C. F. B.

Estimation of Thiocyanic, Hydrocyanic, and Hydrochloric acids. By P. L. JUMEAU (*Bull. Soc. Chim.* [3], 9, 346—351).—Thiocyanates can be titrated with accuracy in the presence of hydrochloric or sulphuric acid by a solution of potassium permanganate, standardised by a solution of ammonium thiocyanate, itself valued by titration with silver nitrate in the usual manner. All the sulphur is converted into sulphuric acid, hydrocyanic acid being liberated; the permanency of the permanganate in the solution marks the end of the titration. If sulphates are to be determined in the liquid, they may be precipitated by barium chloride, after the titration, and the amount of barium sulphate corresponding with the thiocyanate deducted from the weight of the precipitate. If hydrochloric or hydrocyanic acid has to be estimated in a liquid as well as thiocyanic acid, one part of the solution may be precipitated with silver nitrate and the precipitate weighed, whilst the thiocyanic acid is determined in another portion by the method indicated. Or the silver precipitate may be dissolved in hot ammonia, the silver precipitated by hydrochloric acid, and the thiocyanic acid determined by titration in the filtrate. Should thiocyanic, hydrocyanic, and hydrochloric acids have to be all estimated in the same solution, the silver precipitate from one portion of it is treated as described above, in order to estimate the thiocyanic acid. The silver precipitate from another portion is treated by the Kjeldahl process, Nordhausen sulphuric acid and metallic mercury being used in place of the ordinary strong sulphuric acid and mercuric oxide; by this means the nitrogen of the cyanide and thiocyanate is estimated as ammonia; as the thiocyanate has been already estimated, the cyanide may be calculated; the weight of the chloride in the silver precipitate is determined by difference. The hydrochloric acid may also be estimated directly by oxidising the thiocyanic acid in the original solution by potassium permanganate, in the presence of sulphuric acid, expelling the hydrocyanic acid by ebullition, preferably in the presence of zinc, and precipitating the hydrochloric acid with silver nitrate. A. G. B.

Detection of Free Salicylic acid in Salicylaldehyde and Methylsalicylic acid. By A. SCHNEEGANS and J. E. GEROCK (*Zeit. anal. Chem.*, 32, 363; from *Pharm. Centralhalle*, 33, 40).—The violet colour produced by ferric salts in solutions of salicylaldehyde and methylsalicylic acid disappears on the addition of ether, chloroform, amyl alcohol, ethylic acetate, carbon bisulphide, light petroleum, paraffin oil, benzene, toluene, or xylene, whilst that produced by salicylic acid remains. To detect the free acid in artificial winter-green oil, the substance is shaken with 500 parts of water, and to 100 c.c. of the liquid is added 1 c.c. of a highly-dilute ferric chloride solution. If, on the addition of 5 c.c. of chloroform, the violet colour disappears, salicylic acid is absent, but in presence of 0.02 milligram, the colour will still remain visible when seen against a white background. M. J. S.

Analysis of Tobacco. By V. VEDRÖDI (*Zeit. anal. Chem.*, **32**, 277—296).—The author has submitted to an experimental study each step in the methods of Kosutány and Kissling respectively for the estimation of nicotine.

Kosutány's method consists in freeing the tobacco from ammonia by mixing with lime and exposing over acid, then washing out the free nicotine with cold water, transferring it from the watery extract to light petroleum by shaking, then removing from the petroleum solution by shaking with N/10 sulphuric acid, and titrating the excess of acid. In Kissling's method, the tobacco is mixed with weak alcoholic soda and extracted in a Soxhlet's apparatus with ether; the ether is distilled off, and the residue, mixed with strong soda solution, is distilled with steam, when the nicotine passes over and is titrated in the distillate.

The chief source of error in Kosutány's method is that the petroleum does not completely abstract the nicotine from its aqueous solution. The results obtained by Kissling's method are, on the other hand, too high, unless care be taken to get rid of ammonia completely before exhausting with ether, since the ammonia is but partially removed during the evaporation of the ether, and consequently accompanies the nicotine in the subsequent distillation with steam. Moreover, certain of the nitrogenous constituents of the tobacco are dissolved by the soda, and during the distillation yield ammonia.

M. J. S.

Detection of "Saccharin" in Beer. By F. GANTTER (*Zeit. anal. Chem.*, **32**, 309—312).—The author confirms Börnstein's statement that Remsen's reaction can be employed for the detection of "saccharin" in spite of the fact that resorcinol, when heated alone with sulphuric acid, yields a trifling green fluorescence. The fluorescence produced by "saccharin" is so intense that it is visible with a degree of dilution which conceals that produced by resorcinol (*Abstr.*, 1888, 760; and 1889, 449). The test cannot, however, be applied directly to an ethereal extract of beer residue, since this extract contains a substance seemingly a resin, which gives the green fluorescence with as great intensity as "saccharin" itself. Other methods of detection, such as fusion with alkali carbonate and nitrate, and examination for sulphates, and the salicylic acid reaction, are useless, on account of the small quantity of the "saccharin" to be tested for. The following method, however, seems trustworthy:—Half a litre of beer is evaporated to a syrup and, after the addition of a few drops of hydrochloric acid, is shaken in a stoppered bottle with 200 c.c. of 95 per cent. alcohol. The clear solution decanted from the precipitate is evaporated and the residue is shaken with ether. The ethereal extract is evaporated and the residue boiled with water. The aqueous solution when evaporated leaves the "saccharin" in a sufficiently pure condition to allow of its recognition by its intensely sweet, characteristic taste, this taste never being observed in the residue from pure beer.

M. J. S.

General and Physical Chemistry.

Refractive Powers for a Ray of Infinite Wave-length. By R. NASINI (*Gazzetta*, 23, i, 347—353).—The author gives a summary and critique of recent work on refraction constants calculated for the ray A of infinite wave-length. W. J. P.

Specific Inductive Capacities and Refraction Constants. By S. PAGLIANI (*Gazzetta*, 23, i, 537—552).—Maxwell has shown that the specific inductive capacity, K , and the refractive index for a ray of infinite wave-length, μ_∞ , of any substance are in the relation $K = \mu_\infty^2$; if, however, the electrical resistance is infinite, a condition which holds approximately for organic compounds, it follows, from the electro-magnetic theory of light, that the refractive index is independent of the wave-length; the dispersion may hence be disregarded. Joubin has enunciated a connection between the molecular weight, M , and the refractive index, μ , of a substance, which may be resolved into the following expression,

$$\mu - 1 = C \sqrt{\frac{M}{N}},$$

where N is the number of atoms in the molecule and C is a constant. Now, taking Gladstone's refraction formula $\frac{\mu - 1}{d}$ and substituting this value in the equation for the specific inductive capacity given above, Joubin's expression becomes

$$\frac{K - 1}{K} \sqrt{\frac{N}{M}} = C_1 \dots\dots\dots (1).$$

Similarly, using Ketteler's refraction formula $\frac{\mu^2 - 1}{\mu^2 + x} \cdot \frac{1}{d}$, and putting $x = 0$, the expression

$$\frac{K - 1}{K} \cdot \frac{N}{U} = C_2 \dots\dots\dots (2),$$

is obtained, in which U is the molecular volume.

The values of C_2 , calculated for a long series of organic substances of different types, are more concordant than those of C_1 , and both are more constant than the values of C_3 , calculated by Landolt and Jahn from the equation

$$\frac{K - 1}{d(K + 2)} = C_3 \dots\dots\dots (3).$$

The agreement of the values C_2 for homologous series is very close. By transposing equation 2, so as to obtain an expression for K , it is seen that, in a homologous series, K and M should change in the same sense; owing probably to the small differences between the values of

K and the experimental errors incurred in its determination, several exceptions are to be noted amongst the hydrocarbons.

If K is eliminated from equations 1, 2, and 3, expressions containing only μ_{∞} , M, N, U, and a constant may be readily obtained; on calculating the constants from these, it is found that the expressions derived from equations 1 and 2 give more concordant results than that from equation 3.

W. J. P.

Electromotive Force in Electrolytic Analysis. By H. FREUDENBERG (*Zeit. physikal. Chem.*, 12, 97—124).—It has been shown that different values of the electromotive force are necessary to electrolytically decompose aqueous solutions of different salts. In some cases, the electrolytic separation of two metals from a mixed solution of their salts may be effected by choosing an electromotive force just sufficient to decompose one salt, but insufficient to decompose the other. The author has made a large number of experiments on this subject, and has succeeded in effecting the separation, in acid solution, of various metals which show normal decomposition values of the electromotive force. Thus, silver may be separated from arsenic and bismuth; mercury from copper, bismuth, and arsenic; and, finally, copper and bismuth from cadmium and arsenic. Solutions with abnormal decomposition values were also investigated, without practical result in the case of the oxalates, phosphates, and ammonium double salts. Cyanides and sulpho-salts, however, often give methods of separation. For example, silver may be separated from antimony, and mercury from copper and cadmium in potassium cyanide solution, and mercury may be separated from antimony and arsenic in ammoniacal solution.

J. W.

Influence of Boric acid on the Electrical Conductivity of Aqueous Solutions of Organic Acids. By G. MAGNANINI (*Gazzetta*, 23, i, 197—251; compare Abstr., 1892, 256, 1625).—The author confirms his previous conclusions with regard to the influence of boric acid on the electrical conductivity of organic acids, and has further investigated the change in electrical conductivity produced by adding boric acid to solutions of β -hydroxypropionic, hydroxybutyric, α -hydroxyvaleric, trichlorolactic, levulinic, malic, hydrochelidinic, cineolic, pyromucic, isodehydracetic, hydroxydehydracetic, mesoxalic, tartronic, mucic, pyrrolinecarboxylic, acetylpyrrolinecarboxylic, *n*-methyl- α -pyrrolineglyoxylic, phenylpyrrodiazolic, meconic, trichlorodiketopentamethylenehydroxycarboxylic, meta- and para-hydroxybenzoic, ortho- and para-nitrosalicylic, protocatechuic, ortho-, meta-, and para-cresotinic, orthocoumaric, hippuric, caffèic, cuminocarboxylic, paraxyloncarboxylic, benzyleresotinic, β -resorcilic, pyrogallolcarboxylic, tropic, vanillic, guaicolcarboxylic, opianic, diphenylglycollic, apionylketonic, quinic, and parahydroxyquinolineorthocarboxylic acids. The electrical conductivity of acids which do not contain hydroxyl in addition to a carboxyl group is never increased by adding boric acid to their aqueous solutions. Hydroxy-acids which contain the hydroxyl group in the α -position relatively to the carboxyl, whether open or closed chain compounds, always undergo an increase in

electrical conductivity on the addition of boric acid to their aqueous solutions; this rule seems to be obeyed independently of the other groups present in the molecule, and holds whether the hydroxyl group is attached to a primary, secondary, or tertiary carbon atom. In general, no augmentation in electrical conductivity is observed with acids containing an hydroxyl group in any but the α -position to the carboxyl; the reverse is true, however, with gallic and protocatechuic acids.

W. J. P.

Constitution of Metalamine Salts. By A. WERNER and A. MIOLATI (*Zeit. physikal. Chem.*, **12**, 35—55).—The molecular conductivity of equivalent solutions of luteocobaltic bromide, $\text{Co}(\text{NH}_3)_6\text{Br}_3$, roseocobaltic bromide, $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})\text{Br}_3$, and tetramineroseocobaltic bromide, $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2\text{Br}_3$, varies very slightly (from 442 to 417 for μ_{2000}), so that the substitution of water for ammonia in the salts has no marked direct effect on their basic properties. The molecular conductivities of bromopurpureocobaltic bromide, $[\text{CoBr}(\text{NH}_3)_5]\text{Br}_2$, and of xanthocobaltic bromide, $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Br}_2$, are not much greater than half those of the luteo- and roseo-salts. When bromotetraminepurpureocobaltic bromide, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]\text{Br}_2$, is dissolved in water, the violet solution changes gradually into pink, the conductivity at the same time increasing. This is due to the gradual conversion of the salt into tetramineroseocobaltic bromide by a process of hydration. Other examples of similar changes were observed.

Hexaminecobaltic nitrite, $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$, and platosemidiamine chloride are practically non-electrolytes; platosamine chloride conducts slightly. In the case of many of the platinum compounds, the conductivity rises from a very small amount to considerable proportions on standing.

Double salts, such as Erdmann's compound, $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{K}$, give numbers for the conductivity which correspond with the assumption of a dissociation into two ions.

The author's results, in general, confirm the conclusions arrived at, on purely chemical grounds, as to the distribution of the positive and negative groups with regard to the metallic atom in the molecule.

J. W.

Electrical Furnace. By SALADIN (*Bull. Soc. Chim.* [3], **9**, 133—136).—The principle of this apparatus is the same as that of the electrical cautery. A platinum spiral, rendered incandescent by means of a current of electricity, is placed in a vessel of refractory material, and the whole enclosed in a cast-steel case. A side opening in the case communicates with a pump and manometer, and admits of the pressure being increased to 1000 atmospheres; the range of temperature is 1500—1800°, and is measured by a platinum-rhodium couple. Details of the construction of the furnace are given in the original paper.

J. B. T.

Fusion and Volatilisation of Metals and Oxides in the Electric Arc. By H. MOISSAN (*Compt. rend.*, **116**, 1429—1434).—In order to condense and collect the substances that sublime, a copper U-tube, through which a rapid current of cold water is continually

passing, is introduced into the electric furnace immediately above the crucible containing the substance under investigation. Asbestos cardboard placed above the opening through which the U-tube is introduced serves also to condense some of the vapour.

When magnesium pyrophosphate is submitted for five minutes to the action of the arc formed by a current of 300 ampères and 65 volts, a sublimate of magnesium oxide and ordinary phosphorus is obtained. Asbestos, with 300 ampères and 75 volts, almost completely volatilises in a few minutes, and leaves only a small residue of the fused silicate, together with a small globule of magnesium silicide.

Copper, with 350 ampères and 70 volts, volatilises rapidly, and condenses in globules. The vapour forms cupric oxide in contact with air. Silver readily enters into ebullition, and distils more easily than zirconia or silica. It condenses in fused globules, a grey, amorphous powder, and arborescent fragments. Platinum melts almost immediately, and very soon begins to volatilise, condensing in brilliant globules and also in the form of a powder. Aluminium, with 250 ampères and 70 volts, likewise volatilises, and condenses in small spherules. Tin, with 380 ampères and 80 volts, volatilises readily, and condenses in small globules and in fibrous masses. Gold, with 360 ampères and 70 volts, volatilises to a considerable extent, even in six minutes, and condenses in small spheres. Manganese, with a current of 380 ampères and 80 volts, volatilises very readily; 400 grams of the metal left only a small residue of the carbide after heating for ten minutes. Iron, with 350 ampères and 70 volts, volatilises, and condenses as a grey powder mixed with some very brilliant, malleable scales. Uranium, with 350 ampères and 75 volts, volatilises readily, and condenses in small, non-magnetic spheres free from carbon.

Silicon volatilises with 380 ampères and 80 volts, and condenses in small spheres, mixed with a grey powder and a small quantity of silica. Carbon, with 370 ampères and 80 volts, rapidly changes into graphite and then volatilises, condensing in very light, thin, translucent, maroon-coloured plates, similar to or identical with the maroon-coloured variety of carbon observed by Berthelot. It burns easily in oxygen.

Calcium oxide, with 350 ampères and 70 volts, volatilises after 8 or 10 minutes, and with 400 ampères and 80 volts it volatilises in five minutes. The oxide condenses entirely as an amorphous powder. With 1000 ampères and 80 volts, 100 grams of the volatilised oxide can be obtained in five minutes.

Magnesium oxide is more difficult to volatilise than calcium oxide, and its boiling point is near its melting point. With 360 ampères and 80 volts, it gives off a quantity of vapour; and with 1000 ampères and 10 volts, distillation becomes very rapid.

C. H. B.

Discoverer of the Method of determining the Density of Solids by Suspension. By W. OSTWALD (*Zeit. physikal. Chem.*, 12, 94).—The author points out that the discoverer of the method of finding the density of solids by suspension is not Dufour, as Retgers

states, but Davy, who determined (in 1808) the specific gravity of sodium by finding the proportions in which sassafras oil (sp. gr. 1.096) and naphtha (sp. gr. 0.861) must be mixed in order to produce a liquid in which the metal remains suspended without sinking or floating.

J. W.

Formation of Supersaturated Solutions. By A. L. POTILITZIN (*J. Russ. Chem. Soc.*, **25**, 73—75).—The following rule regarding the formation of supersaturated aqueous solutions is stated by the author. Only those saline hydrates can form supersaturated solutions whose dissociation tension in dry air at the ordinary temperature is considerable. Salts containing water of crystallisation, which do not decompose at the ordinary temperature in dry air or in a vacuum, or decompose only very slowly, are incapable at that temperature of giving supersaturated solutions.

The behaviour of the chlorates and bromates of the alkaline earths is cited in illustration.

J. W.

Influence of Hydration on Solubility. By N. S. KURNAKOFF (*J. Russ. Chem. Soc.*, **24**, 629—631).—Le Chatelier stated the rule that when a substance forms two hydrates, the hydrate containing least water is more soluble than the higher hydrate at any temperature below the point of transformation. The author finds a great number of apparent exceptions to this rule amongst the ammonio-metallic compounds. For example, the chlorides and nitrates of the roseopentamine bases $\text{MX}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$ (where $\text{M} = \text{Co}, \text{Cr}, \text{or Ir}$) are much more soluble than the corresponding anhydrous forms $\text{MX}_3 \cdot 5\text{NH}_3$, the purpureopentamine salts. He also mentions the fact that organic anhydrides (acid anhydrides, lactones, oxides, &c.) are less soluble in water than the corresponding hydrated compounds.

The following solubilities were found by V. Meyer's method for various ammonia compounds of cobalt.

Temp.	100 parts of water dissolve		
	$\text{CoCl}_3 \cdot 5\text{NH}_3$.	$\text{CoCl}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$.	$\text{CoCl}_3 \cdot 6\text{NH}_3$.
0°	0.232	16.12	4.26
16.9°	—	24.87	—
46.6°	1.031	—	12.74

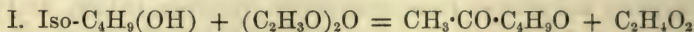
J. W.

Non-electrolytic Dissociation in Solutions. By M. WILDERMANN (*Ber.*, **26**, 1773—1786).—In salt solutions the author recognises two sorts of dissociation, electrolytic dissociation into ions and a non-electrolytic dissociation of larger molecular aggregates of the dissolved substance into smaller. Thus, in a solution of potassium chloride, the following substances may be assumed to exist, K_2Cl_2 , KCl , K_2Cl , KCl_2 , K^+ , and Cl^- . The author is of opinion that this additional assumption of non-electrolytic dissociation is sufficient to explain the divergencies existing between the observed data and the values calculated on the electrolytic dissociation hypothesis alone.

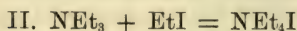
In the present paper, he discusses the electrical conductivity of salt solutions which do not in general obey the dilution law applicable to weak acids and bases. From an imperfect mathematical discussion, based on the above assumption, he deduces formulæ which show a qualitative agreement with the experimental data. J. W.

The Colour of the Ions. By G. MAGNANINI (*Zeit. physikal. Chem.*, **12**, 56—72).—Ostwald, from his researches on the absorption spectra of solutions of the permanganates, rosolates, chromoxalates, &c., drew the conclusion that the absorption depended on the colour of the ions in the solution and not on that of the undissociated molecules of the dissolved salt, for all permanganates, for example, gave precisely the same absorption in dilute solutions. The author contests this conclusion, and shows that the salts of violuric acid give red solutions, whilst violuric acid itself gives colourless aqueous solutions, although it is dissociated to the extent of 8 per cent. at a dilution of 256. It cannot, therefore, be the negative ion which causes the absorption in the salt solution, nor can it be the positive metallic ion; so that the colour must come from the undissociated part. The absorption for equivalent solutions of potassium, sodium, and ammonium violurates is equal. Addition of large excess of potassium nitrate to a solution of potassium violurate does not influence the absorption, although it diminishes the degree of dissociation. J. W.

Influence of Dilution on the Velocity of Chemical Reactions. By V. OMELYANSKY (*J. Russ. Chem. Soc.*, **24**, 647—663).—The author has investigated the influence of dilution on the velocity constant of two reactions, namely:—



in benzene solution, and



in acetone solution.

In the first column of the following table is given the dilution V, in the second the velocity constant K, and in the third their product. The measurements were made at 100°.

I.

V.	K.	KV.
1.0 (without solvent)	0.212	0.212
2.0	0.178	0.356
4.0	0.123	0.492
6.0	0.102	0.612
16.0	0.0401	0.641
40.9	0.0165	0.674
61.6	0.0107	0.659
79.8	0.00875	0.698
101.0	0.00682	0.692
149.6	0.00457	0.682
303.7	0.00220	0.668

II.

V.	K.	KV.
16.0	0.0676	1.08
40.9	0.0280	1.14
61.0	0.0209	1.27
80.3	0.0159	1.27
100.8	0.0122	1.11
151.2	0.00805	1.21

From these tables it appears that after the reacting substances have been diluted with 15 times their volume of solvent, the constant of velocity of a bimolecular reaction is inversely proportional to the dilution.

J. W.

Vapour Tensions of Solutions of Sulphur and Phosphorus in Carbon Bisulphide. By G. GUGLIELMO (*Real. Accad. Linc.*, 1892, ii, 210—216).—The author has measured the vapour tensions of solutions of sulphur and phosphorus in carbon bisulphide by enclosing them in a space exhausted by a Sprengel pump, and measuring the vapour pressure by means of a manometer. For solutions at ordinary temperatures, a glass apparatus was used consisting of two bulbs, one to contain pure carbon bisulphide, the other to hold the solution; these vessels could be isolated from each other and from the pump by means of suitably-arranged mercury traps. In such an apparatus, the vapour tension of the pure carbon bisulphide is first determined, then that of the solution; the ratios of the differences of the two pressures to the vapour tension of carbon bisulphide at the corresponding temperatures are therefore proportional to the number of dissolved molecules per unit of solution. In the case of sulphur, the experiments were conducted between 0° and 13.8°, and show that for solutions up to 20 per cent., the molecular depression of the vapour tension corresponds with a sulphur molecule containing 8 atoms for the more dilute solutions, increasing to 9 for the more concentrated.

The vapour tensions of several carbon bisulphide solutions of phosphorus were measured at 0°; the depressions of the vapour tensions correspond approximately with a tetratomic molecule for dilute solutions (3 per cent.), just as is found by vapour density determinations. As would be expected, the molecular weight increases for more concentrated solutions.

The solutions are kept stirred by means of steel rods, which are enclosed in the exhausted bulbs, and are moved up and down by the motion of a horseshoe magnet outside.

W. J. P.

Determination of Molecular Weights by Beckmann's Method. By G. BARONI (*Gazzetta*, 23, i, 263—277).—In this preliminary communication, the author gives a number of data for the boiling points of aqueous solutions of boric acid, potassium chloride and bromide, sodium chloride, and barium chloride. The immediate continuation of the investigation is interrupted by an accident.

W. J. P.

Phenanthrene as a Solvent in Cryoscopic Determinations.

By F. GARELLI and A. FERRATINI (*Gazzetta*, 23, i, 442—452).—The authors have previously suggested (*Abstr.*, 1892, 156) that the abnormal values deduced from cryoscopic determinations of the molecular weight of indole in naphthalene solution, result from the formation of solid solutions of indole in the crystallising hydrocarbon; they suspected also that the formation of such solid solutions was in some way influenced by similarity of constitution between the solvent and the dissolved substance. It is now found that the crystals which separate on cooling a liquid solution of carbazole in phenanthrene, two substances of very analogous constitution, contain a large quantity of the dissolved substance; the crystals deposited from a liquid solution containing 7.5 per cent. of carbazole contained 11.42 per cent. of the latter, whilst a 7.5 per cent. solution of diphenylamine in phenanthrene deposited crystals containing only 5.39 per cent. of the amido-compound.

The abnormally small depressions of the freezing points of hydrocarbons and allied compounds by benzoic acid have been remarked by several investigators. Benzoic acid also gives too small a depression of the freezing point of phenanthrene, and the authors suppose that this may be found a general rule for organic acids.

Apart from the great difficulty experienced in purifying phenanthrene, the authors consider it a better solvent for use in cryoscopic determinations than naphthalene; its high constant of depression (120) renders it possible to work accurately with very dilute solutions, whilst its small tendency to volatilise makes it more easy of manipulation than naphthalene. A satisfactory series of test experiments with naphthalene, diphenylamine, thymol, stilbene, metadinitrobenzene, and *n*-methylcarbazole is given in illustration of this.

W. J. P.

Cryohydric Temperatures. By F. A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 12, 73—93).—Guthrie made some experiments on the cryohydric points of systems of mixed salts, but did not arrive at any general conclusion. The author now discusses the question from the theoretical standpoint, and makes the following deductions.

When the two salts do not form a double salt, the cryohydric point of the mixture is lower than the cryohydric point of a solution in equilibrium with either of the salts separately. This conclusion receives confirmation both from Guthrie's and from the author's experiments.

When a double salt is formed which decomposes on dissolution, such as $\text{PbI}_2 \cdot \text{KI} \cdot 2\text{H}_2\text{O}$, the cryohydric temperature of a solution in equilibrium with the double salt and one of its components is lower than the cryohydric temperature of a solution in equilibrium with this component alone; and the cryohydric point of a solution in equilibrium with the double salt and the component which is not deposited is lower than that of a solution in equilibrium with the double salt and the component which is deposited.

When a double salt is formed which dissolves homogeneously without decomposition, such as $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, the cryohydric temperature of a solution in equilibrium with the double salt

and one of its components is lower than the cryohydric temperature of a solution of the double salt alone.

These conclusions have been confirmed by experiment. J. W.

Osmotic Pressure. By A. NACCARI (*Gazzetta*, 23, i, 535—537).—A porous cell, containing a semi-permeable membrane of copper ferrocyanide and fitted with a manometer, is partially filled with sugar solution and placed in pure water; water then passes into the cell, and the osmotic pressure set up is measured by the manometer. The cell is now placed in a more concentrated sugar solution than that which it contains, and water passes out; by reducing the atmospheric pressure in the cell, equilibrium is established between the internal and external sugar solutions, although the pressure inside is not so great as the osmotic pressure set up when the cell stood in pure water and contained the same volume of solution. The author concludes from this experiment that if Boyle's law were applicable to liquid solutions, it should be possible for a gas at constant volume and temperature to exert any given pressure, and that hence the theory of osmotic pressures is faulty. W. J. P.

Note by Abstractor.—The osmotic pressure in such experiments as the above is, of course, measured by counterbalancing it against an equal and known gaseous pressure; consequently, in the second part of the author's experiment the pressure registered on the manometer is simply the difference of the osmotic pressures of the two sugar solutions which are in equilibrium, and nothing is proved against the theory of osmotic pressures. W. J. P.

Relation between the Periodic Classifications of L. Meyer and Mendeléeff. By U. ALVISI (*Gazzetta*, 23, i, 509—517).—The author endeavours to trace a relation between the equivalents and specific gravities of the elements by means of the differences of the numerical values of these two functions. W. J. P.

Specific Gravities of the Elements in the Periodic System. By U. ALVISI (*Gazzetta*, 23, i, 518—523).—In L. Meyer's or Mendeléeff's classification of the elements, the sum of the specific gravities of the elements on one half of any period is approximately equal to the sum of those on the other half. W. J. P.

Stereochemistry or Motochemistry? By E. MOLINARI (*J. pr. Chem.* [2], 48, 113—135).—By the term "motochemistry," the author implies the hypothesis that the constitution of compounds is dependent on the intramolecular movements of the atoms in relation to each other, rather than on the relative positions of the atoms in space. The hypothesis treats the bonds by which it is customary to represent the union of atoms as signifying the nature of the swing or energy of the atoms with regard to each other. Thus, doubly linked and singly linked carbon atoms are of different value in respect of the energy of their movement with regard to each other, and double or treble bonds signify excess of energy, ready to be exerted in saturating the com-

pound. The author applies his hypothesis to the benzene ring, and shows that only one ortho-bi-substitution product is possible. Motoisomerism involves asymmetry, but the term must be used in a greatly extended sense, the phenomenon depending on the mass and valency of the atoms or atomic groups, as well as on their number and nature. Motoisomerides will exist in those cases in which it is possible for the order of approachment of the (in this sense) asymmetrical carbon atom towards its neighbouring atoms to vary. Thus, in the case of benzilmonoxime, $\text{COPh}\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{OH} \\ \text{C}_6\text{H}_5 \end{smallmatrix}$, it is possible for two motoisomerides to exist; for if the swing between carbon and carbon be designated by a , and that between carbon and nitrogen by b , the isomerides will be represented by (1) a, a, b, b , and (2) a, b, a, b .

The author adduces a number of other examples of the application of this hypothesis.

A. G. B.

Inorganic Chemistry.

Iodine Monochloride. By S. TANATAR (*J. Russ. Chem. Soc.*, **25**, 97—101).—To prepare the β -modification of iodine monochloride of melting point $13\cdot9^\circ$, the author places the liquid chloride in a vessel with a drawn-out neck, and heats very slowly so that the walls become covered with crystals of the trichloride. The heating is continued until the boiling point of the liquid is reached and all the trichloride expelled through the constricted neck, which is then sealed off. On cooling, first to the atmospheric temperature and afterwards to -10° , no trichloride should be deposited on the upper parts of the vessel. If any such separation takes place, the boiling must be renewed, for no β -monochloride can be formed in presence of trichloride. When the β -modification is once formed, it is very stable as long as it is kept in the sealed vessel. When melted and cooled in a sealed tube to -20° , it passes into the α -modification, from which it may be re-obtained by again melting and cooling to -10° .

The heat of transformation of the β -chloride into the α -modification is $0\cdot273$ Cal., and the heat of fusion of the α -chloride is $-2\cdot32$ Cal. The sp. gr. of liquid iodine monochloride is $3\cdot2856$ at $16^\circ/16^\circ$ and $3\cdot2402$ at $34^\circ/34^\circ$.

J. W.

Densities of the Principal Gases. By Lord RAYLEIGH (*Proc. Roy. Soc.*, **53**, 134—149).—The author describes in some detail the manometric gauge, and the connections of the globe with pump and manometer, which he has employed in his new experiments on the densities of air, oxygen, and nitrogen.

The oxygen was prepared in three ways—(a) from chlorates, (b) from potassium permanganate, and (c) by electrolysis. The air

drawn from outside was passed through potash solution, then through tubes filled with fragments of solid potash, and finally over phosphoric anhydride. The nitrogen was prepared by passing air through a potash solution, over reduced copper, then through a U-tube to deposit water, again over heated copper, and finally over heated copper oxide. The following table is given of the densities of oxygen, nitrogen, and hydrogen referred to that of air as unity.

	Oxygen.	Nitrogen.	Hydrogen.
Regnault (corr.).....	1·10562	0·97138	0·06949
v. Jolly (corr.)	1·10502	0·97245	—
Leduc	1·1050	0·9720	0·06947
Rayleigh	1·10535	0·97209	0·06960
Mean.....	1·10525	0·97218	0·06952

The density of hydrogen was calculated from that of oxygen, using the ratio 15·882. The mean of the best densities under standard conditions referred to water at 4° as 1000, that is, the weight of 1 litre in grams, is:—

Air.	Oxygen.	Nitrogen.	Hydrogen.
1·29347	1·42961	1·25749	0·08991

J. W.

Electrolysis of Steam. By J. J. THOMSON (*Proc. Roy. Soc.*, **53**, 90—110).—A current of steam was passed through the middle limb of a T-tube, the closed side limbs of which were furnished with delivery tubes, and also with gold or platinum electrodes between which sparks might be passed through the steam. The delivery tubes conducted the gases into two endimeters, in which the gaseous mixture formed on passage of the sparks was exploded. When the sparks were from 1·5 to 4 mm. long it was observed that, within the limit of error of the experiment, the volumes of the excess of hydrogen in the one tube and of oxygen in the other, which remain after the explosion of the mixed gases, are respectively equal to the volumes of the hydrogen and oxygen liberated in a water voltameter placed in series with the steam tube; and that the excess of hydrogen appears in the tube which is in connection with the positive electrode, the excess of oxygen in the tube which is in connection with the negative electrode. When the spark length is greater than 4 mm., the first of the preceding results ceases to hold, and when the spark length is increased to over 11 mm., the excess of hydrogen, instead of appearing at the positive electrode, changes over to the negative, the excess of oxygen at the same time going over from the negative to the positive electrode. When the sparks are very much longer, about 22 mm., reversal again takes place, the hydrogen appearing at the positive electrode.

The author finds that when the arc discharge passes through hydrogen and oxygen respectively, the hydrogen behaves as if it had a negative charge, and the oxygen as if it had a positive one.

J. W.

Composition of Water by Volume. By A. SCOTT (*Proc. Roy. Soc.*, **53**, 130—134).—The author has continued his investigation of

the proportions by volume in which oxygen and hydrogen unite, using improved apparatus. The taps were lubricated with syrupy phosphoric acid instead of vaselin, which was found to introduce traces of the oxides of carbon into the gases; and the measurements were all made at constant volume by varying the pressure. The oxygen was prepared from silver oxide, and the hydrogen from sodium and steam. In some experiments the hydrogen was further treated by absorption in palladium.

The mean ratio of hydrogen to oxygen was found in 5 series of 53 experiments to be :—

2·002435 \pm 0·00006, impurity in both gases equally,
or 2·002431 \pm 0·00006, „ hydrogen alone.

If six experiments were rejected, the value would be 1·002466 \pm 0·000003, any impurity making no difference, whether assumed to be all in the hydrogen or equally distributed between the two gases. The most probable value is 2·00245, which, combined with Rayleigh's value, 15·882, for the ratio of the densities of the gases, gives 15·862 for the atomic weight of oxygen, hydrogen being 1, and 1·0078 for the atomic weight of hydrogen, oxygen being taken as 16. J. W.

Density, &c., of Sulphurous Anhydride. By A. LEDUC (*Compt. rend.*, 117, 219—222).—Under normal conditions of pressure and temperature, the density of gaseous sulphurous anhydride is 2·2639, with an estimated error of 1/10,000th of the value. The gas investigated was prepared from pure sulphuric acid and pure mercury, in an apparatus without rubber connections, and was dried with sulphuric acid and phosphoric anhydride.

The author finds the following formula to express the relation between the weight of the gas at a pressure p (from 1 to 0·5 atmosphere) and that at the normal pressure.

$$W_{760} = W_p \frac{760}{p} [1 + 323 \times 10^{-7}(760 - p)].$$

The mean coefficient of expansion of the gas between 0° and 20° at normal pressure was found to be 0·00396, the true coefficient at 0° being 0·003978. Under a pressure of 334 mm. the mean coefficient of expansion is 0·003787 between 0° and 22°. The coefficient of increase of pressure with the temperature is 0·003883 at 0°.

J. W.

Preparation of Ammonium Persulphate. By K. ELBS (*J. pr. Chem.* [2], 48, 185—189; compare Marshall, *Trans.*, 1891, 771).—A porous clay cell (80—100 c.c. capacity), containing a saturated solution of ammonium sulphate in a mixture of 1 part by volume of sulphuric acid with 8 parts by volume of water, is placed in a beaker and surrounded by a mixture of equal volumes of sulphuric acid and water. A lead cylinder, placed round the porous cell, serves as the cathode, and a platinum spiral having a surface of 0·5 sq. cm. is suspended inside the porous cell to serve as the anode. The beaker is imbedded in ice. The electrolysis is effected by a current of 2—3

ampères ; some 8 volts will be necessary when the internal resistance of the decomposing cell is about 1 ohm. After 2—3 hours, the contents of the porous cell are filtered through glass wool and the crystals of ammonium persulphate dried on a porous plate ; the filtrate is shaken with ammonium sulphate and once more electrolysed. 20—40 grams of the persulphate may thus be obtained in one operation, the yield being least at the outset, when the liquid is being saturated with the persulphate. The sulphuric acid in the outer cell eventually becomes alkaline from the transit of the ammonium ion, and *pari passu* the ammonium sulphate in the inner cell becomes strongly acid ; from time to time the former liquid must be renewed and the latter nearly neutralised with ammonia. To recover the persulphate left in the liquor when the preparation has been completed, a concentrated solution of potassium carbonate or acetate is added ; potassium persulphate will thus be precipitated, as 100 parts of water only dissolve 2 parts of this salt, whereas they dissolve 65 parts of the ammonium salt.

Ammonium persulphate, thus prepared, contains some 3—5 per cent. of impurities, consisting chiefly of ammonium sulphate, but partly of ammonium alum, derived from the clay of the porous cell. It may be recrystallised from water. A. G. B.

Atomic Refraction of Boron. By A. GHIRA (*Gazzetta*, 23, i, 452—462).—The author has determined the refraction constants of a number of compounds of boron for the line D and the α , β , and γ hydrogen lines ; the results obtained for the D and H_α lines are summarised in the following tables.

Substance.	Temp.	$P \frac{\mu_D - 1}{d}$.	$P \frac{\mu_D^2 - 1}{d(\mu_D^2 + 2)}$.	Atomic refraction of boron.	
				From μ .	From μ^2 .
$B(OEt)_3$	6.2°	63.30	38.57	5.04	3.24
$B(OC_4H_9^\beta)_3$	7.8	109.68	66.31	5.52	3.37
$B(OC_5H_{11}^\beta)_3$	9.7	132.60	79.88	5.49	3.12
$B(OC_3H_5)_3$	8.3	84.18	50.69	3.87	2.73

Substance.	Temp.	$P \frac{\mu_{H_\alpha} - 1}{d}$.	$P \frac{\mu_{H_\alpha}^2 - 1}{d(\mu_{H_\alpha}^2 + 2)}$.	Atomic refraction of boron.	
				From μ .	From μ^2 .
BCl_3	5.7°	34.62	20.86	5.32	2.80
BBr_3	—	51.03	29.69	5.13	2.84
$B(OEt)_3$	6.2	63.00	38.41	5.10	3.19
$B(OC_4H_9^\beta)_3$	7.8	109.13	66.01	5.63	3.43
$B(OC_5H_{11}^\beta)_3$	9.7	131.90	79.50	5.60	3.24
$B(OC_3H_5)_3$	8.3	83.83	50.32	3.73	2.32

The author also gives the refraction for the rays H_β and H_γ , and thence calculates the dispersion for H_α — H_γ . The specific gravities employed are referred to water at 4° ; the atomic refractions of other elements than boron, used in the calculations for the hydrogen lines, are those of Nasini and Costa (Abstr., 1891, 1305), for the D line those of Conrady and Zecchini (this vol., ii, 253).

The author has also made observations on aqueous solutions of boric anhydride; little weight, however, attaches to these results, owing to the fact that less than 2 per cent. solutions had to be employed.

W. J. P.

Combination of Boron Bromide with Phosphorus Tribromide. By TARBLE (*Compt. rend.*, 116, 1521—1524).—Boron bromide was prepared in large quantity by the action of bromine on amorphous boron, obtained by Moissan's method of reducing boric anhydride by means of magnesium. In presence of carbon bisulphide, it combines readily with phosphorus tribromide in molecular proportion, forming the compound $PBr_3 \cdot BBr_3$, which separates in beautiful, colourless needles after half the solvent has been distilled off and the residual liquid is cooled. These crystals melt at about 61° , dissolve in carbon bisulphide and in chloroform, fume in moist air, and are very easily decomposed by water with formation of boric, phosphorous, and hydrobromic acids. When heated in a current of hydrogen, it sublimes with partial decomposition; in a current of oxygen, it decomposes slightly at the ordinary temperature, and takes fire below a red heat. Sulphur, bromine, iodine, and other non-metals are without action on it, but chlorine at the ordinary temperature converts it into the compound $PCl_3 \cdot BCl_3$.

Boron phosphorus bromide crystallises unchanged from both phosphorus tribromide and boron bromide, and hence would seem to be the only stable compound of these two substances.

The compound $PBr_3 \cdot BBr_3$ is obtained in small, white crystals by pouring a carbon bisulphide solution of phosphorus pentabromide into a similar solution of boron bromide. It is only slightly soluble in cold carbon bisulphide, but dissolves readily on heating, and can be recrystallised from this solvent. When heated in sealed tubes, it melts at 140° ; but when heated with exposure to air, it volatilises at about 105° without melting. When exposed to the air, it fumes, and it is energetically decomposed by water, with formation of boric, phosphoric, and hydrobromic acids. Pure and dry hydrogen is without action on it even when heated, but it burns when heated to redness in oxygen, and is completely decomposed by chlorine with great development of heat. It absorbs ammonia at the ordinary temperature with development of heat, and yields a white, crystalline compound. No evidence could be obtained of the existence of any other compound of phosphorus pentabromide and boron tribromide.

C. H. B.

Bromoborates. By G. ROUSSEAU and H. ALLAIRE (*Compt. rend.*, 116, 1445—1446; compare this vol., ii, 468).—Iron bromoborate, $6FeO \cdot 8B_2O_3 \cdot FeBr_2$, is readily obtained by passing bromine vapour

over an intimate mixture of boronatrocalcite with a large excess of fragments of iron wire heated to redness. It forms a mixture of greyish-white cubes and octahedra which act on polarised light in the same way as natural crystals of boracite, and are larger the higher the temperature. They are mixed with black prisms of ferric borate, which can be removed by treatment with cold, concentrated hydrobromic acid. Iron bromoborate dissolves slowly in warm nitric acid.

Zinc bromoborate, $6\text{ZnO}, 8\text{B}_2\text{O}_3, \text{ZnBr}_2$, forms white, microscopic, pseudo-cubic crystals, which also act on polarised light. It is obtained by the action of zinc bromide vapour on calcium borate, heated to redness in an atmosphere of carbonic anhydride.

C. H. B.

Cyclic Condensation of Carbon. Artificial Production of the Diamond. By G. ROUSSEAU (*Compt. rend.*, 117, 164—167).—When barium and strontium manganites are heated, they undergo a cyclic change, a salt such as MnO_2, BaO being formed at 800° , changing to $2\text{MnO}_2, \text{BaO}$ at $1000\text{--}1200^\circ$, and reverting again to MnO_2, BaO at a white heat. A similar change occurs when sodium manganite is heated. By treating hydrocarbons in this manner, it seemed probable, since each of the modifications of carbon is known to have a temperature or zone of temperature of maximum stability, that an analogous change might be produced, and this proved to be the case. Acetylene was generated from calcium carbide and steam in a lime crucible, heated in an electric furnace; after $1\frac{1}{2}$ hours, several particles of black diamond were found to have been formed; whilst in the cooler parts of the crucible, graphite was deposited in black, microscopic leaflets, identical with those of natural plumbago. In a second experiment, the carbide was decomposed by moist coal gas, the decomposition of which furnished an additional supply of acetylene; 20 milligrams of diamond was obtained.

The diamonds, some of which were as much as 0.5 mm. in diameter, formed wrinkled, brownish-black, roundish masses, sometimes covered with white, brilliant points, more or less crystalline in character. They remained unattacked by potassium chlorate and nitric acid mixture, by potassium hydrogen sulphate, and by hydrofluoric acid. They scratched corundum, and, when burned, left a cellular ash. It is noteworthy that the formation took place under atmospheric pressure.

J. N. W.

Solubility of "Insoluble" Salts. By A. F. HOLLEMAN (*Zeit. physikal. Chem.*, 12, 125—139).—The author has investigated the electrical conductivity of aqueous solutions of the so-called insoluble salts, and from his numbers calculates the actual solubility.

In the case of precipitated calcium sulphate, the dilution (in equivalents) of the saturated solution was found to be $v = 36.9$ at 15° , whilst by evaporation and weighing, $v = 37.4$ was obtained. Other check determinations gave equally concordant results.

The following are the values obtained:—

1 part of BaSO ₄	dissolves in	429,700 parts of water at 18·4°
"	"	320,000
" SrSO ₄	"	10,070
"	"	10,030
" AgCl	"	715,800
"	"	384,100
" AgBr	"	1,971,650
"	"	775,400
" AgI	"	1,074,040
"	"	420,260
" CaC ₂ O ₄ ·2Aq	"	148,220
"	"	124,400
" BaCO ₃	"	64,070
"	"	45,566
" SrCO ₃	"	121,760
"	"	91,468
" CaCO ₃	"	99,500
"	"	80,040

From the solubilities at the different temperatures, the heats of precipitation were calculated, the results showing fair accordance with the observed thermochemical values.

J. W.

Method for reducing Metallic Oxides. By W. H. GREENE and W. H. WAHL (*Chem. News*, 68, 3—4).—For the production of alloys, the use of metallic silicides is suggested as more beneficial than reduction by carbon. For example: 128 lbs. of a metallic alloy having the composition Fe, 70; Mn, 29; C, 0·7; Si, trace, may be obtained by melting on the furnace hearth or in a crucible a charge of 100 lbs. of ferrosilicon (containing Si, 10 per cent., and C, 1 per cent.), and adding 70 lbs. of manganous oxide and 50 lbs. of lime. The reaction takes place quickly, the silicon seizing the oxygen of the manganous oxide and fluxing with the lime, manganous oxide, and alumina present; therefore, the manganous oxide has to be added in larger quantity than is required by theory. By substituting other oxides for the manganous oxide, ferro-alloys have been obtained containing 50 per cent. of nickel, or 20 per cent. of chromium, or 50 per cent. of tungsten; in all these, the carbon may be reduced so low as to meet all requirements of commerce. The method is applicable to other metals besides iron.

D. A. L.

Action of Carbonic Oxide on Sodammonium and on Potass-ammonium. By A. JOANNIS (*Compt. rend.*, 116, 1518—1521).—When pure and dry carbonic oxide is passed into a solution of potassammonium in liquefied ammonia at about -50°, the blue colour gradually becomes weaker, and at last changes to pink. At this point the reaction is complete, and if the ammonia is allowed to evaporate, the compound *potassium carbonyl*, K₂C₂O₂, is obtained as a pale, rose-coloured powder which detonates in contact with air or water, or when heated to 100°. If, however, it is allowed to come in

contact with water vapour in a vacuum, it deliquesces and forms a yellow solution.

Sodium carbonyl, $\text{Na}_2\text{C}_2\text{O}_2$, is a white powder with a lilac tint, and is obtained in a similar manner. It detonates at 90° , or when brought in contact with air or water, but deliquesces quietly in contact with water vapour in a vacuum. When it detonates, very little gas is evolved, and a small quantity of sodium cyanide is formed, but the principal reaction is represented by the equation $2\text{Na}_2\text{C}_2\text{O}_2 = \text{Na}_2\text{CO}_3 + \text{Na}_2\text{O} + \text{C}_3$. When detonation takes place in presence of water, the small quantity of gas evolved contains 86 per cent. of hydrogen and 14 per cent. of carbonic oxide. C. H. B.

Quantitative Separation of Cæsium and the Preparation of Pure Cæsium and Rubidium Compounds. By H. L. WELLS (*Zeit. anorg. Chem.*, **4**, 341—345; and *Amer. J. Sci.*, **46**, 186).—The solubility of the double salt Cs_2PbCl_6 in a solution of equal parts of fuming hydrochloric acid and water, saturated with chlorine and containing twice the theoretical quantity of lead chloride, is 0.000068 gram Cs_2PbCl_6 for 1 c.c. In concentrated hydrochloric acid, in the presence of excess of lead chloride, the solubility is 0.000049 gram per c.c. Under the same conditions, the solubility of the salt Rb_2PbCl_6 is 0.003 gram per c.c. From a solution containing cæsium and potassium, the cæsium is precipitated as Cs_2PbCl_6 by chlorine in the presence of lead chloride and hydrochloric acid, and the precipitate dried at 100° , and weighed; or decomposed by hot water, and the cæsium determined in the filtrate as sulphate. The results are about 4 per cent. too low.

From a solution containing cæsium, rubidium, potassium, sodium, and lithium, the cæsium and rubidium are precipitated as the double salts, with lead tetrachloride, dried at 100° , and weighed; then converted into the sulphates, and again weighed. The determinations of the cæsium are fairly good. Part of the rubidium, however, remains in the solution, and can be precipitated, together with the potassium, by means of platinic chloride.

The preparation of pure cæsium and rubidium salts from their minerals is carried out as follows: They are first separated in the form of the double salts with lead tetrachloride; the latter are decomposed with water, the solution treated with a slight excess of ammonium sulphide to free it from lead, and the filtrate evaporated to dryness; the mixed chlorides of cæsium and rubidium are dissolved in concentrated nitric acid, the solution evaporated to dryness, the residue dissolved in water, excess of oxalic acid added, and the mixture again evaporated to dryness and heated in a platinum crucible until the oxalates are completely converted into carbonates. The rubidium is then separated as acid oxalate, and the cæsium as cæsium antimony chloride. E. C. R.

Action of Zinc and Magnesium on Solutions of Metallic Salts. Estimation of Potassium. By A. VILLIERS and F. BORG (*Compt. rend.*, **116**, 1524—1527).—Estimations of metals such as copper and platinum, by precipitating them from solutions of their

salts by means of metallic zinc, are usually inaccurate, even when the zinc is pure, in consequence of the formation of alloys of variable composition.

Magnesium behaves differently, and can be used for the accurate estimation of copper, gold, and platinum, provided the solution contains no other metals except those of the alkalis and alkaline earths. The copper, &c., is precipitated in a granular form which is easily washed. In presence of metals other than those specified, alloys are formed even in a strongly acid solution.

This reaction can be applied to the estimation of potassium. The platinumochloride is precipitated, washed with a mixture of equal volumes of absolute alcohol and ether, then dissolved in hot water, acidified with hydrochloric acid, and gradually mixed with excess of magnesium. The precipitated platinum is washed, heated, and weighed. The method is very accurate, and can be applied to the impure platinumochloride obtained by the precipitation of various commercial potassium compounds, when the weight of the salt would give inaccurate results, whilst the weight of reduced platinum gives accurate results. This is true also of precipitates formed in the presence of bromides.

C. H. B.

Ternary Alloys. Part VII. By C. R. A. WRIGHT (*Proc. Roy. Soc.*, 52, 530—543; compare this vol., ii, 415).—The author has prepared a number of alloys consisting of lead or bismuth, aluminium or zinc, and cadmium or antimony, molten lead, bismuth, and zinc being miscible with cadmium or antimony in all proportions. The close analogy previously noted between aluminium and zinc is not shown in these alloys, partly because cadmium and aluminium (contrary to statements in text-books) are not completely miscible, and partly because aluminium and antimony form a compound, AlSb , which melts at 1045° ; the discussion of these alloys is therefore postponed for the present. In the case of the mixtures of lead, zinc, and cadmium, the ratio of lead and zinc corresponds with the formula Pb_4Zn , and that of lead and cadmium to Pb_2Cd . The composition at the limiting point was: lead, 36.5; zinc, 2.9; cadmium, 60.6. At the limiting point of the mixture of bismuth, zinc, and cadmium, the composition was: bismuth, 19.5; zinc, 28.5; cadmium, 52.0, corresponding with a ratio represented by the formula BiZn_3 . A comparison of the critical curves of this and the preceding alloy shows that the substitution of bismuth for lead depresses the curve. In the case of the mixtures of lead, zinc, and antimony, the values at the limiting point were: lead, 38.1; zinc, 35.4; antimony, 26.5; the ratio of lead to zinc corresponding with the formula PbZn_3 . The composition of the analogous bismuth alloy at the limiting point was: antimony, 17.50; bismuth, 22.75; zinc, 59.75, corresponding with the formula BiZn_3 ; in this case, the limiting point coincided with the highest point of the curve; further, the curve with cadmium as solvent lies outside the one deduced with tin as solvent, that with antimony as solvent inside; the temperature of experiment in all three series being $600\text{—}650^\circ$.

J. B. T.

Double Chlorides of Lead and Ammonium. By W. W. RANDALL (*Amer. Chem. J.*, **15**, 494—504).—André (Abstr., 1883, 717, 903) has described a number of double chlorides of ammonium and lead whose formulæ are not in accord with the law which Remsen has enunciated as controlling the composition of double haloid salts (Abstr., 1889, 934). The author has endeavoured to prepare the double salts described by André, but in most cases crystallographic examination showed that the substances prepared were mixtures, not individual compounds. The only salts which appeared homogeneous under the microscope were $2\text{PbCl}_2 \cdot \text{NH}_4\text{Cl}$ and $\text{PbCl}_2 \cdot 2\text{NH}_4\text{Cl}$, both of which are in accord with Remsen's law. A. G. B.

Double Salts of Lead Tetrachloride. By H. L. WELLS (*Zeit. anorg. Chem.*, **4**, 335—340, and *Amer. J. Sci.*, **46**, 180).—The salts are yellow and crystallise in regular octahedra. They are decomposed by water with the formation of lead peroxide and chlorine. The caesium salt is less readily decomposed than the others. They are also decomposed by boiling with excess of hydrochloric acid; and in this case also the caesium salt is decomposed less readily. The caesium salt is almost insoluble in concentrated solutions of caesium chloride and in hydrochloric acid in the presence of free chlorine. The salts can be washed with hydrochloric acid containing chlorine, and are not decomposed by exposure to air. The corresponding sodium and calcium salts could not be prepared.

Ammonium plumbichloride, $(\text{NH}_4)_2\text{PbCl}_6$, is prepared by adding a cold, saturated solution of ammonium chloride in dilute hydrochloric acid to a solution prepared by dissolving lead peroxide in hydrochloric acid at 0° .

Potassium plumbichloride, K_2PbCl_6 , is obtained by mixing equal volumes of a saturated solution of potassium chloride and lead chloride in hydrochloric acid saturated with chlorine, and of a similar solution, which does not contain potassium chloride.

Rubidium plumbichloride, Rb_2PbCl_6 , is obtained by treating a solution of rubidium chloride and lead chloride in dilute hydrochloric acid with chlorine at 20° .

Cæsium plumbichloride, Cs_2PbCl_6 , is easily obtained by treating a solution of lead chloride and excess of caesium chloride with chlorine. The salt is usually of a lemon colour, but is dark brown if prepared in the presence of strong hydrochloric acid and a large excess of lead chloride. The lemon-coloured salt crystallises in isolated octahedra; the brown salt in octahedric groups of octahedra.

E. C. R.

Ammonium Lead Haloïds. By H. L. WELLS and W. R. JOHNSTON (*Amer. J. Sci.*, **46**, 25—34).—A recent investigation (Abstr., 1892, 773) of the caesium lead and potassium lead haloïds having established the existence of four very simple types of double salts, the authors re-investigated the ammonium lead haloïds, of which a considerable number, with very complicated formulæ, have been described. All of the extremely complicated ammonium lead salts were prepared by André (Abstr., 1883, 717, 903), and the authors are convinced that not one of the 11 salts described by him

exists. The authors' results show that the ammonium-lead haloïds are strictly analogous to the potassium salts. Their work has resulted in the preparation of the following series of salts :—

Type 2 : 1.	Type 1 : 1.	Type 1 : 2.
—	$3\text{NH}_4\text{PbCl}_3, \text{H}_2\text{O}$	$\text{NH}_4\text{Pb}_2\text{Cl}_5$
$(\text{NH}_4)_2\text{PbBr}_4, \text{H}_2\text{O}$	—	$\text{NH}_4\text{Pb}_3\text{Br}_5$
—	$\text{NH}_4\text{PbI}_3, 2\text{H}_2\text{O}$	—
		B. H. B.

Halogen Compounds of Potassium and Lead. By H. L. WELLS (*Zeit. anorg. Chem.*, **4**, 346—351, and *Amer. J. Sci.*, **46**, 190).—A compound, to which the author assigns the composition $\text{K}_3\text{Pb}_2\text{I}_8, 4\text{H}_2\text{O}$, is precipitated from saturated solutions of potassium iodide containing iodine and lead iodide. It is stable on exposure to air, is decomposed by water and alcohol, and crystallises in lustrous, black prisms. The salt contains 16·5 per cent. of potassium iodide, but has not been obtained pure.

The *bromide*, $\text{K}_3\text{Pb}_2\text{Br}_8, 4\text{H}_2\text{O}$, is obtained by adding bromine to a saturated solution of potassium bromide and lead bromide, and allowing the mixture to remain over night. It crystallises in dark brown prisms, is very unstable, and evolves bromine on exposure to air.

A stable, bright red salt is obtained in a similar manner from a solution containing free iodine and bromine in molecular proportions. It contains the halogens in the proportion 23Br : I.

The *salt*, $\text{K}_3\text{Pb}_2(\text{BrI})_8, 4\text{H}_2\text{O}$, is obtained by adding bromine to a concentrated solution of potassium iodide containing lead iodide. It crystallises in dark, bronze-coloured prisms. As both this salt and the iodide mentioned above crystallise in tetragonal prisms, the author assigns the above composition to the iodide. E. C. R.

Rubidium Lead Haloïds. By H. L. WELLS (*Amer. J. Sci.*, **46**, 34—38).—The cæsium lead, potassium lead, and ammonium lead haloïds having been studied in the author's laboratory, an investigation of the rubidium salts has been made in order to make the work more complete. The salts prepared and described are :—

- 2 : 1-Rubidium lead chloride, $2\text{Rb}_2\text{PbCl}_4, \text{H}_2\text{O}$.
- 1 : 2-Rubidium lead chloride, RbPb_2Cl_5 .
- 2 : 1-Rubidium lead bromide, $2\text{Rb}_2\text{PbBr}_4, \text{H}_2\text{O}$.
- 1 : 2-Rubidium lead bromide, RbPb_2Br_5 .
- 1 : 1-Rubidium lead iodide, $\text{RbPbI}_3, 2\text{H}_2\text{O}$.

B. H. B.

Dissociation of Calcium Plumbate. By H. LE CHATELIER (*Compt. rend.*, **117**, 109—110).—The dissociation pressures of calcium plumbate at different temperatures are as follows :—

T°	880°.	940°.	956°.	1020°.	1060°.	1070°.	1100°.	1110°.
Pressure in mm.	47	112	117	350	557	570	940	1040

A higher temperature is required than in the case of barium peroxide, but, on the other hand, calcium plumbate has the advantage of

absorbing oxygen more rapidly, and, moreover, it does not require the moisture and carbonic anhydride to be removed from the air.

C. H. B.

Spectrum of Thallium. By H. WILDE (*Proc. Roy. Soc.*, **53**, 369—372).—Huggins observed a line in the spark spectrum of thallium to which he assigned the wave-length 6547 on Angström's scale; but the existence of this line was not confirmed by subsequent observers. The author shows that the line actually exists, but is almost coincident with the hydrogen line, C 6562, for which it has been mistaken. The real wave-length is λ 6560, so that thallium has two well-marked lines, λ 6560, 5349, corresponding with the lines of indium, λ 4510, 4101, and gallium, λ 4170, 4031. The spaces between the pairs of homologous lines increase with the atomic weight.

J. W.

Copper Fluorides. By POULENC (*Compt. rend.*, **116**, 1446—1449).—The action of hydrofluoric acid on hydrated cuprous oxide yields metallic copper and a solution of cupric fluoride, and in this respect resembles the action of sulphuric acid on the same oxide.

Anhydrous cuprous fluoride, Cu_2F_2 , can, however, be obtained by the action of hydrogen fluoride on cuprous chloride heated to dull redness. The action is not complete until the temperature is raised to 1100—1200°, the point at which cuprous fluoride volatilises. It can also be prepared by heating anhydrous cupric fluoride at 600° in a current of hydrogen fluoride, the temperature being raised to 1100—1200° towards the close of the operation.

Cuprous fluoride which has been fused is a ruby-red, transparent substance with a crystalline fracture. When exposed to the air, it is converted into cupric fluoride and becomes blue; in contact with water this change takes place more rapidly. It is insoluble in alcohol of 90°; dissolves in boiling hydrochloric acid, but is not, like cuprous chloride, precipitated when the solution is diluted. It is only slightly attacked by sulphuric acid, even when heated, but nitric acid acts on it with great energy, nitrogen oxides being evolved. When heated in presence of air, cuprous fluoride is converted into cupric oxide, and it is easily reduced by hydrogen at a red heat.

Cupric fluoride is obtained as a white, amorphous powder by the action of fused ammonium fluoride on the hydrated cupric fluoride, but this powder readily becomes crystalline when heated in hydrogen fluoride at 500°. The fluoride is also obtained directly in small, white crystals by heating cupric oxide, or hydrated cupric fluoride, at 400° in a current of hydrogen fluoride. If the temperature exceeds 500°, the compound is decomposed.

When exposed to air, the fluoride becomes blue owing to absorption of water, and it likewise becomes blue when placed in ether or alcohol which contains water. It is very readily dissolved by hydrochloric, nitric, and hydrofluoric acids, is very easily reduced by hydrogen, and when heated at 300° with exposure to air, it is completely converted into cupric oxide. Water vapour converts it into copper oxide and hydrogen fluoride; hydrogen sulphide converts it into cupric sulphide and hydrogen fluoride, and hydrogen chloride converts it into cupric chloride.

When heated above 500° , it yields cuprous fluoride, but no evidence of the evolution of free fluorine could be obtained. The dissociation is not complete below 1100 — 1200° .
C. H. B.

Cuprous Phosphide. By A. GRANGER (*Compt. rend.*, 117, 231—232).—When red phosphorus is immersed in an ammoniacal solution of copper sulphate, it becomes coated, as is well known, with a greyish deposit, which is a mixture of cuprous phosphide and metallic copper; the same occurs with an ammoniacal solution of copper phosphate, but the transformation is never complete, even at 100° . If, however, red phosphorus is heated with a large excess of copper phosphite and water in a sealed tube for four hours at 130° , its entire conversion is effected. The product is washed quickly with aqueous ammonia and water in succession, and dried in a vacuum. If the temperature has not exceeded that specified, it is not contaminated with metallic copper.

Cuprous phosphide, Cu_2P_2 , is a grey powder resembling plumbago in appearance. It is attacked by chlorine and bromine in the cold, and is readily dissolved by dilute acetic acid; a mixture of it with potassium nitrate or chlorate detonates violently when struck. When heated in contact with air, it is oxidised to copper phosphate. It is decomposed by heat into products identical with those yielded by cupric phosphide (*Abstr.*, 1892, 410). It is slightly soluble in hydrochloric acid, yielding a solution from which cuprous oxide is precipitated by potash, and which, when supersaturated with ammonia, precipitates metallic silver from an ammoniacal solution of silver nitrate.
JN. W.

Simple Nature of Samarium. By E. DEMARÇAY (*Compt. rend.*, 117, 163—164).—An examination of the absorption spectra of four samarium fractionations, prepared by Boisbaudran, gave practically identical results, the slight differences being due to the presence of traces of neodymium and erbium. The doubt thus cast on the hypothesis of the dual nature of samarium has been confirmed by a re-examination of the work leading to that hypothesis. The samarium band is resolved when the nitrate is examined with a sufficiently fine slit into two bands, $\lambda = 415$ and 419 , and neodymium nitrate proves to exhibit a band of feeble, vague character, $\lambda =$ about 418 , intermediate between these two. A variable percentage of neodymium in the samarium salt, together with a slit of varying width, are thus sufficient to account for the supposed variability of the samarium band, $\lambda = 415$ — 419 .
JN. W.

Samarium. By L. DE BOISBAUDRAN (*Compt. rend.*, 117, 199—201; compare *Abstr.*, 1892, 780).—The samarium bands vary in relative intensity with experimental conditions. Thus the band Z_{ζ} ($\lambda = 614.4$ — 611.2) is strengthened relatively to the orange band by hydrochloric acid, and by other means, so that the increase in intensity of this band observed in the head fraction of an ammonia fractionation may have been due merely to change of conditions. A renewed examination of the head and middle fractions of this frac-

tionation showed a markedly diminished difference, which further successive fractionations with ammonia and oxalic acid failed to increase. In the head and tail fractions of the last fractionation, the band Z_{ζ} was, however, slightly less intense than in the middle fraction of the first fractionation.

An additional nebulous band in the green (wave-length of maximum intensity $\lambda = 535.4$) is described; this is increased somewhat in intensity when the spark is very short, or when it impinges on the edge of the surface of the liquid instead of on the middle, and is also increased in intensity by acids. It is a little more intense in the head than in the middle fraction of the first ammonia fractionation. The most marked contrast it offers in behaviour to the band Z_{ζ} is that the latter is weakened or even obliterated by acetic acid.

JN. W.

Manganous Sulphide. By U. ANTONY and P. DONNINI (*Gazzetta*, 23, i, 560—567).—Manganous sulphide is thrown down from ammoniacal manganous solutions by ammonium sulphide as a pink precipitate, which the older workers supposed to be a hydrated sulphide; the authors show, however, that if it be collected, washed in an atmosphere of hydrogen sulphide, and dried at 70° in a current of carbonic anhydride, it has the composition MnS . The sulphide thus obtained consists of tiny, reddish, transparent crystals, and is contaminated with a little sulphur, which may be extracted by treatment with carbon bisulphide; its sp. gr. at $17^{\circ}/17^{\circ}$ is 3.55.

If the red precipitate be well washed, and left in a solution of ammonium sulphide for a few days, it turns green; the same change is also brought about by heating the red powder at 300 — 320° . The green modification is crystalline, and has the same composition as the red, but a somewhat higher sp. gr., namely, 3.63, referred to water at 17° . Neither modification loses sulphur on heating.

W. J. P.

Influence of Electricity on the Carburization of Iron by Cementation. By J. GARNIER (*Compt. rend.*, 16, 1449—1451).—A bar of steel containing only 0.1 per cent. of carbon and a rod of gas carbon were placed end to end in a refractory tube, and well insulated. The tube was then heated at 900 — 1000° , and a current of 55 ampères and 7 volts was passed from the carbon to the steel. After three hours, it was found that that part of the iron opposed to the carbon cut glass easily, and a section showed that cementation had taken place to a depth of about 10 mm., whilst the carbon was corroded at the surface of contact.

Two bars of steel were then packed side by side in wood charcoal with a space of 10 mm. between them, and were heated at 900 — 1000° for three hours, a current of 55 ampères and 2.5 volts being passed from one to the other. It was found that the bar which served as the anode was practically unaffected, whilst in that which played the part of the cathode cementation had occurred to a considerable depth.

It would seem, therefore, that at about 1000° the cementation of iron

takes place with very great rapidity under the influence of a comparatively weak electric current.

C. H. B.

Oxidation of Nickel Sulphide. By P. DE CLERMONT (*Compt. rend.*, 117, 229—231).—When freshly precipitated, well-washed nickel sulphide is exposed to the air in a moist condition on filter paper, it gradually loses its moisture, and after 24 to 48 hours assumes an apple-green colour. The green product is extracted with water, and the insoluble residue dissolved in dilute hydrochloric acid. The acid solution is found to contain the basic sulphate $\text{NiSO}_4 \cdot 6\text{NiO}$. The aqueous solution becomes greener on further exposure to the air, and is found to contain a mixture of the basic sulphate, the normal sulphate, and the sulphide, together with free sulphur.

When the sulphide is exposed under a layer of water several centimetres in depth, the oxidation proceeds more slowly, extending over months, whilst the relative amounts of the insoluble product and of basic sulphate in the latter are much diminished. Carbonic anhydride is also freely absorbed.

Since the sulphide dissolves in the sulphate (though only in the presence of sulphur) to form a stable compound, the oxidation of nickel sulphide is never complete under the conditions described above.

JN. W.

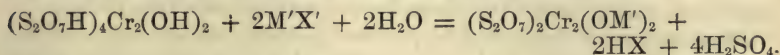
Potassium Tetrachromate and Ammonium Tetrachromate.

By G. WYROUBOFF (*Bull. Soc. Chim.* [3], 9, 156).—The author prepared and described in 1881 (*Bull. Soc. Min.*, 4, 17) the potassium and ammonium tetrachromates obtained by G. C. Schmidt (compare this vol., ii, 16).

J. B. T.

Chromopyrosulphuric acid. By A. RECOURA (*Compt. rend.*, 117, 37—40 and 101—103).—When a solution containing 1 mol. of chromic sulphate and 5 mols. of sulphuric acid is evaporated on a water bath, a deep green, syrupy liquid is obtained, and if this is heated for one or two days at 110—115°, it solidifies in brittle, vitreous, transparent lamellæ, much paler in colour than the liquid. These crystals consist of *chromopyrosulphuric acid*, $(\text{S}_2\text{O}_7\text{H})_4\text{Cr}_2(\text{OH})_3$, derived from pyrosulphuric acid in the same way as chromosulphuric acid (this vol., ii, 470) is derived from sulphuric acid. It is very soluble in water, forming an opaline yellowish-green solution, very different in appearance from solutions of chromosulphuric acid, and this liquid has the remarkable property of yielding a flocculent, greenish-white precipitate, with solutions of any metallic salts, including those of sodium, potassium, and ammonium. Copper sulphate, for example, yields a greenish-white precipitate of the composition $\text{CuCr}_2\text{S}_4\text{O}_{14}$, but this, when boiled with a quantity of sodium hydroxide equivalent to the sulphuric acid that it contains, yields an insoluble green compound, which is copper chromite. The author concludes that in chromopyrosulphuric acid the hydroxyl groups are in direct union with the chromium, and the constitution of the copper salt is $(\text{S}_2\text{O}_7)_2\text{Cr}_2(\text{O}_2\text{Cu})$. With alkali metals, the reaction is similar,

and in all cases 4 mols. of sulphuric acid are liberated, together with the acid in the precipitant, the general equation being



All the precipitates are insoluble.

When solutions of alkalis are added to a solution of chromopyrosulphuric acid, a greenish-white precipitate forms, and the liquid becomes neutral when 10 equivalents of alkali have been added for each molecule of the salt. The alkali hydroxides yield the same precipitate as the corresponding salts, and the acid seems to be decabasic in consequence of the liberation of the 4 mols. sulphuric acid.

The salts $(S_2O_7)_2Cr_2(OM')_2$ are *pyrosulphochromites*.

Pyrosulphochromic Hydroxide.—If concentrated nitric, hydrochloric, or sulphuric acid is added to a solution of chromopyrosulphuric acid, a gelatinous greenish-white precipitate of pyrosulphochromic hydroxide is formed; this dissolves in pure water, and its solution precipitates all metallic salt solutions. The same product is obtained by heating chromopyrosulphuric acid at $140-150^\circ$, until it no longer loses weight. It is a slightly greenish, grey powder, and its solution is greenish-grey, and very opaline. It has already been shown that certain pyrosulphochromites yield chromites, and it is noteworthy how the association of chromous acid, $Cr_2O_2(OH)_2$, with the radicle S_2O_7 accentuates the acidic function of the hydroxyl groups.

It is remarkable that although pyrosulphochromic hydroxide, $(S_2O_7)_2Cr_2(OH)_2$, and chromosulphuric acid, $(SO_4)_2Cr_2(SO_4H)_2$, are isomeric, the salts of the former are all insoluble, whilst those of the latter are very soluble. The salts of the former are, however, converted into chromosulphates by prolonged boiling with water. The pyrosulphochromites yield chromites when treated with sodium hydroxide.

Chromopyrosulphuric acid loses 4 mols. SO_3 when heated at 140° , whereas chromotrisulphuric acid loses no SO_3 at 150° , and this fact agrees with the constitution already attributed to the former acid.

C. H. B.

Action of Gaseous Ammonia on Molybdenyl Chloride. By E. F. SMITH and V. LENHER (*Zeit. anorg. Chem.*, **4**, 374—380).—A compound of the formula $Mo_5O_8N_3H_3$ is obtained by treating molybdenyl chloride, MoO_2Cl_2 , with dry ammonia. Much heat is developed during the action, and ammonium chloride and water are formed. The compound has a black, metallic appearance, and is stable in the air; it does not combine with hydrochloric acid, but is energetically attacked by nitric acid (sp. gr. 1.42), slowly by dilute alkalis, and yields ammonia when fused with potassium hydroxide. When heated in an atmosphere of nitrogen, water is formed, and a red compound is obtained, which is probably molybdenum dioxide mixed with a small quantity of nitride. When treated with aqueous silver nitrate, crystals of metallic silver are deposited.

When molybdenyl chloride is heated to bright redness in an atmosphere of ammonia, an amorphous, black, metallic-looking mass is obtained, which has the composition $Mo_7O_{14}N_5H_{10}$. It is not attacked

by dilute alkalis, gives ammonia when fused with potassium hydroxide, is energetically converted into molybdic acid by the action of nitric acid, and precipitates silver from a solution of silver nitrate.

Other products have been obtained; their composition varies according to the time and temperature at which the action takes place.

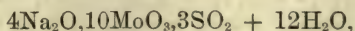
E. C. R.

Combination of Molybdates with Sulphurous acid. By E. PÉCHARD (*Compt. rend.*, **116**, 1441—1444).—In the absence of other inorganic acids, sulphurous acid does not reduce solutions of molybdates, but yields a series of complex compounds.

If sulphurous anhydride is passed into a warm and moderately concentrated solution of ammonium molybdate until the liquid smells strongly of the gas, *ammonium molybdosulphite*, $4(\text{NH}_4)_2\text{O}, 10\text{MoO}_3, 3\text{SO}_2 + 6\text{H}_2\text{O}$, separates in colourless, microscopic octahedra, which act on polarised light. It is readily decomposed by heat, both when solid and when in solution, and it is only slightly soluble in water.

Potassium molybdosulphite, $4\text{K}_2\text{O}, 10\text{MoO}_3, 3\text{SO}_2 + 10\text{H}_2\text{O}$, is obtained in a similar manner by passing sulphurous anhydride into a solution of potassium bimolybdate, prepared by the action of potassium carbonate on molybdic acid. It forms beautiful, amber-coloured, prismatic crystals, which lose water and sulphurous anhydride when heated. *Potassium ammonium molybdosulphite*, $4\text{KNH}_4\text{O}, 10\text{MoO}_3, 3\text{SO}_2 + 9\text{H}_2\text{O}$, is obtained by adding potassium bromide to a solution of ammonium molybdate previously saturated with sulphurous anhydride, and separates in long, yellow needles. It is only slightly soluble in water, and, when the solution is heated, sulphurous anhydride is given off, and potassium hydrogen molybdate separates.

When a solution of sodium hydrogen molybdate is saturated with sulphurous anhydride, and allowed to evaporate in a vacuum, it first deposits aggregations of lamellæ of the composition



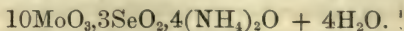
and afterwards colourless, very efflorescent octahedra of another hydrate, $4\text{Na}_2\text{O}, 10\text{MoO}_3, 3\text{SO}_2 + 16\text{H}_2\text{O}$.

Attempts to obtain the corresponding barium salt were unsuccessful. When barium chloride is added to a solution of one of the alkali salts, sulphurous anhydride is given off, and a white, crystalline precipitate separates, containing barium molybdosulphite and barium molybdate in proportions which vary with the conditions.

Selenious acid yields analogous, but much more stable, compounds, which will be described subsequently.

C. H. B.

Combination of Selenious acid with Molybdates: Molybdoselenious acid. By E. PÉCHARD (*Compt. rend.*, **117**, 104—107).—When about one-fourth of its weight of selenious anhydride is added to ammonium molybdate in warm aqueous solution, the liquid, on cooling, deposits long, silky needles of the compound



This salt is much more soluble in hot than in cold water, and is

insoluble in alcohol. When heated, it gives off water, ammonia, and selenious anhydride. Hydrochloric acid, when added to an aqueous solution, produces a gelatinous precipitate of ammonium hydrogen molybdoselenite, which dissolves with decomposition in excess of hydrochloric acid.

Potassium molybdoselenite is obtained by the action of selenious anhydride on potassium molybdate, and crystallises with $5\text{H}_2\text{O}$ in colourless, hexagonal tables. It is more soluble in water than the ammonium salt, and is slightly soluble in alcohol. When heated at 440° , it decomposes, with evolution of water and selenious anhydride. A double ammonium potassium salt can be obtained, and crystallises with $5\text{H}_2\text{O}$ in the same form as the potassium salt.

The sodium salt is analogous in composition, but crystallises with greater difficulty in very efflorescent octahedra containing $15\text{H}_2\text{O}$. It is very soluble in water, but insoluble in alcohol.

The barium salt is obtained by mixing hot solutions of barium chloride and one of the preceding salts; it separates, on cooling, in slender needles containing $3\text{H}_2\text{O}$. Lead molybdoselenite is white, and insoluble, even in hot water. The mercurous and silver salts, and the salts of other heavy metals, are amorphous and yellowish.

Molybdoselenious acid is obtained on decomposing the barium salt with sulphuric acid. It forms a yellow solution, which can be evaporated to a syrup, but will not crystallise.

Other compounds of molybdates with selenious acid exist, and the salt $5\text{MoO}_3, \text{SeO}_2, 2(\text{NH}_4)_2\text{O} + 2\text{H}_2\text{O}$ has been obtained as a crystalline, white powder.

C. H. B.

Action of Gaseous Ammonia on Tungstyl Chloride. By E. F. SMITH and O. L. SHINN (*Zeit. anorg. Chem.*, **4**, 381—383).—Tungstyl chloride, WO_2Cl_2 , is not attacked by dry ammonia at ordinary temperatures, but, on heating, a slow reaction sets in and a black mass is obtained, together with ammonium chloride and water. The compound has the composition $\text{W}_4\text{O}_4\text{N}_4\text{H}_2$. It is insoluble in water, is not attacked by hydrochloric acid or dilute alkalis, but is very energetically acted on by concentrated nitric acid, and yields ammonia when fused with potassium hydroxide. It is not altered by heating with concentrated sulphuric acid at 180 — 250° . When treated with aqueous silver nitrate, crystals of metallic silver are deposited.

E. C. R.

Tungstous Oxide associated with Colombous Oxide. By W. P. HEADDEN (*Amer. J. Sci.*, **45**, 280—286).—In a paper on "Iron Tin Alloys" (this vol., ii, 211), the author referred to certain products as iron bottoms, the formation of which he discussed. This paper is a study of the residues obtained from those bottoms. In the residues, as obtained after having been freed from carbon, the author has found a mixture of columbous and tungstous oxides. Tungstous oxide, WO , as thus obtained, crystallises in the hexagonal system, mostly in hemiprisms having a light grey to tin-white colour, a metallic lustre, a hardness greater than glass, and a dark grey streak. The tungstous oxide was probably formed by the action of stannous oxide on metallic

tungsten, which had been reduced in the original tin charge of the furnace.
B. H. B.

Volatilisation of Zirconia and Silica at a High Temperature, and their Reduction by Carbon. By H. MOISSAN (*Compt. rend.*, 116, 1222—1224; compare this vol., ii, 507).—When zirconia is heated in an electric arc with a current of 360 ampères and 70 volts, it rapidly melts, and in about 10 minutes is in complete ebullition, giving off thick, white vapours, which condense to a white powder, consisting of opaque, microscopic granules; these scratch glass, and have all the other properties of zirconia; sp. gr. = 5.10. The residue in the crucible has a crystalline fracture, and dendritic crystals of zirconia are found in the cooler parts of the furnace.

If zirconia is fused in a carbon crucible under the conditions specified, there is found below the non-volatilised oxide a button of zirconium mixed with some zirconia, but free from carbon and nitrogen. If, on the other hand, the zirconia is mixed with excess of carbon, a zirconium carbide is obtained, containing from 4.22 to 5.10 per cent. of carbon. It has a metallic appearance and a brilliant fracture, and, when fused with excess of zirconia, yields pure zirconium, of sp. gr. 4.25, which scratches glass and rubies easily, and closely resembles the zirconium described by Troost. Zirconium carbides containing more than 5 per cent. of carbon inflame somewhat rapidly when exposed to the air.

Silica, in an arc of the same intensity, melts almost immediately, and is in complete ebullition after six or seven minutes. The vapours condense to a slightly bluish, white powder, consisting of a mixture of amorphous silica with small, opalescent spheres, which scratch glass easily; sp. gr. = 2.4. About 20 grams of silica can be volatilised in from 10 to 15 minutes, and the condensed product is very easily attacked by hydrofluoric acid and by alkalis.

Under the conditions specified, silica is reduced by carbon, and yields a crystalline silicon carbide, which is under investigation.

Small spherules of silica, identical in properties with those just described, are found on the inside of glass globes enclosing electric arc-lights.
C. H. B.

Extraction of Zirconium and Thorium. By L. TROOST (*Compt. rend.*, 116, 1428—1429).—The volatilisation of silica in the electric arc (preceding abstract) can be utilised for the separation of silica from zirconia or thoria. Finely powdered zircon is intimately mixed with an excess of finely divided carbon, and compressed into small cylinders, which are placed in a carbon dish, and subjected to the action of an electric arc in a closed vessel through which a current of carbonic anhydride is passed. Silica volatilises very rapidly, together with a thick, black smoke, probably due to the reduction and volatilisation of silicon, which reoxidises outside the electric arc. When the volatilisation ceases, the residue contains only about 1.5 per cent. of silica, whereas the original zircon contains about 33 per cent.

Similar results are obtained with thorite and orangite, silicates of

thorium, and this preliminary separation of the silica greatly facilitates the isolation of the metal.

C. H. B.

Arsenic Chlorosulphides and Antimony Chlorosulphides.

By L. OUVRARD (*Compt. rend.*, 116, 1516—1518).—Dry hydrogen sulphide acts on arsenic trichloride at the ordinary temperature, with evolution of hydrogen chloride and formation of a yellow precipitate, which, if the action is continued until the evolution of hydrogen chloride ceases, and the precipitate is washed with carbon bisulphide, consists partly of crystalline, and partly of amorphous, matter. The proportion of the latter varies, and it can be removed by levigation with carbon bisulphide. Both the amorphous and crystalline products consist of arsenic chlorosulphide, $\text{As}_2\text{S}_5\text{Cl}$. This compound is slowly decomposed by boiling water, with formation of arsenic trichloride and amorphous arsenious sulphide. It melts at about 120° , and volatilises at about 300° (out of contact with air), with decomposition into arsenic trichloride and sulphide.

If the hydrogen sulphide used in the preparation of the chlorosulphide is not quite dry, the product is simply the ordinary sulphide, and the same result follows if the reacting substances are heated.

Arsenious sulphide dissolves in the chloride when heated, but is deposited unchanged on cooling. If, however, a mixture of the two substances is heated in sealed tubes at 150° , the chloride being in excess, the compound AsS_2Cl is obtained in microscopic crystals, which melt and volatilise readily when heated out of contact with air. It is decomposed by water in the same way as the preceding compound, and is dissolved by solutions of ammonia and alkali carbonates.

If 1 part of the sulphide and 5 parts of the chloride are heated at 180° for 24 hours, and cooled slowly, the chlorosulphide, $\text{As}_2\text{S}_5\text{Cl}$, is obtained in very small, pale-yellow crystals.

Antimony trichloride, when treated at its melting point with a limited quantity of dry hydrogen sulphide, yields red-brown crystals of the chlorosulphide SbS_2Cl . It is insoluble in carbon bisulphide, melts readily, and is readily attacked by acids. If the passage of the hydrogen sulphide is continued until hydrogen chloride is no longer given off, the chlorosulphide $\text{Sb}_2\text{S}_5\text{Cl}$ is obtained in small prisms. At a temperature above the melting point of the trichloride, the product of the action of hydrogen sulphide is the ordinary antimony trisulphide.

C. H. B.

Arsenic and Antimony Iodosulphides. By L. OUVRARD (*Compt. rend.*, 117, 107—109).—Dry hydrogen sulphide has no action on arsenic iodide in the cold, but at 200° some of the iodide volatilises, and a crystallised iodosulphide, $\text{As}_2\text{S}_5\text{I}$, remains. The compound AsSI_2 is obtained by heating together out of contact with air arsenic sulphide and excess of iodine, and crystallising the product from carbon bisulphide. If the arsenic sulphide is in excess, the product is the compound AsS_2I , described by Schneider.

A mixture of equal parts of iodine and precipitated antimony sulphide reacts at the ordinary temperature with development of

heat, and after treatment with carbon bisulphide, cinnabar-red needles of the compound SbS_2I are obtained. If 2 parts of iodine and 1 part of the sulphide are heated in a vacuum sealed tube, two products, SbS_2I and SbS_2I_3 , are obtained, and can be separated by taking advantage of their different volatilities. Dry hydrogen sulphide acts readily on antimony iodide at about 150° , and yields reddish-brown crystals of the compound SbS_2I . C. H. B.

Metallurgy of Bismuth. By E. MATTHEY (*Proc. Roy. Soc.*, **52**, 467—472; compare Abstr., 1891, 1161).—The purification of bismuth from arsenic has hitherto been accomplished by fusing it with iron in presence of a flux, the compound of iron and arsenic being then removed as a scum; the method requires considerable time, and involves a serious loss of bismuth by volatilisation. The author finds that the whole of the arsenic can be eliminated by exposing the well stirred alloy, when heated above its melting point, to the action of air. No loss of bismuth occurs. In one experiment, 700—800 kilos. of alloy, containing 0.65 per cent. of arsenic, and melting at 278° , gave up the whole of the arsenic on heating at 395 — 513° . On heating the alloy in a vacuum, the arsenic is volatilised at about the same temperature as when heated in air.

Bismuth may also be completely freed from antimony by prolonged fusion and constant stirring, the antimony oxidising and separating as an oily film; in one experiment an alloy containing 0.80 per cent. of antimony, together with other impurities, was heated for five hours at 350° , and afterwards during about four hours at 458° ; a slight loss of bismuth occurs. The above temperatures were determined by means of Le Chatelier's platinum-rhodium pyrometer. J. B. T.

Gold Crystals containing Mercury. By T. WILM (*Zeit. anorg. Chem.*, **4**, 325—334).—If gold in the form of small reguli, or as a fine powder, is dissolved in mercury under water in such quantities that the amalgam is quite liquid, then warmed for some time on the water-bath, and the amalgam treated with strong nitric acid as long as mercury is dissolved, the gold is recovered as a yellowish-brown powder, which is not crystalline, and contains mercury which cannot be removed by treatment with nitric acid, but is easily expelled by heat.

If in the place of mercury a dilute liquid amalgam of sodium is employed under water, the gold is recovered in bright-yellow, lustrous prisms or needles 2—3 mm. in length. The crystals contain from 5.45 to 11.45 per cent. of mercury, which cannot be entirely removed by boiling with strong nitric acid. When heated, the mercury is expelled, and the gold is obtained in dark coloured cakes, showing its former crystalline texture.

After the dissolution of the gold in the sodium amalgam, the aqueous liquid becomes rose-red, and finally dark-violet. If the mixture of gold amalgam and water is warmed on the water-bath, a bluish-green solution is obtained. These solutions may be exposed to the air at ordinary temperatures without any alteration in colour taking place. When acidified with hydrochloric acid, a black precipitate of pure gold is obtained. The black gold differs from the

ordinary modification in its extreme lightness; also it is soluble in alkaline solutions, and does not amalgamate with mercury or with sodium amalgam. When heated, it yields the ordinary modification as a violet-red powder.

E. C. R.

Mineralogical Chemistry.

Three supposed New Sulphides of Iron and Nickel. By S. L. PENFIELD (*Amer. J. Sci.*, **45**, 494—497).—The author brings forward evidence to show that folgerite, blueite, and whartonite, sulphides of iron and nickel from the Sudbury nickel mines, Ontario, Canada, described by S. H. Emmens, cannot be regarded as distinct species. It is clear that little dependence can be placed on formulæ deduced from analyses of minerals of such doubtful purity, especially where a chief constituent is determined by difference.

B. H. B.

Deposits of Native Soda near Laramie, Wyoming. By H. PEMBERTON, Jun., and G. P. TUCKER (*Chem. News*, **68**, 19—20).—Deposits of sodium sulphate, generally known as the Union Pacific Lakes, are found in a nearly rainless region on the high Wyoming plateau, in the neighbourhood of the town of Laramie. The lower and greater portion of these deposits is of uncertain thickness, and is known as the “solid soda;” it consists of a mass of crystals of a faint greenish colour, mixed with a considerable amount of black, slimy mud; its composition is Na_2SO_4 , 36 per cent.; CaSO_4 , 1.45 per cent.; MgCl_2 , 0.77 per cent.; NaCl , 0.21 per cent.; H_2O , 46.87 per cent.; insoluble residue, 13.86 per cent. The upper portion of the deposits, from 3 to 12 inches thick, is formed by solution from the upper layers of the lower part, and the subsequent evaporation or cooling of the solution; it has the following composition (calculated as anhydrous), Na_2SO_4 , 99.73, and MgCl_2 , 0.26, per cent., with a trace of insoluble matter; the article manufactured in Laramie is, however, not so pure.

Samples of the supernatant water taken from some of these “lakes” or deposits at a time when they were entirely under water gave the following numbers, in grams per litre, on analysis.

	Big Lake.	Track Lake.	Red Lake.
Sp. gr.	1.0487	1.0725	1.0887
Na_2SO_4	44.90	75.63	93.07
CaSO	1.75	1.46	2.01
MgSO	0.60	0.70	1.43
MgCl_2	6.43	3.00	4.16
$\text{Na}_2\text{B}_4\text{O}_7$ (?)	1.46	1.21	0.75
Total solids	55.14	82.00	101.42

The borax represents the results of titration with standard acid using methyl orange as indicator. Samples from two other lakes,

yielded a residue which, when calcined, contained only 43·12 and 69·55 per cent. of sodium sulphate, besides magnesium and calcium sulphates and insoluble matter.

D. A. L.

Ettringite from Tombstone, Arizona. By A. J. MOSES (*Amer. J. Sci.*, **45**, 489—492).—The author has examined several specimens of ettringite from the Lucky Cuss mine, Tombstone, Arizona. The mineral occurs in white, radiating fibres; it has a sp. gr. of 1·55, and fuses readily before the blowpipe. It thus differs from Lehmann's ettringite in that the latter occurs in acicular, hexagonal crystals, has a sp. gr. of 1·75, and is said to be infusible. Analysis gives results corresponding with the formula $(\text{H}_{22}\text{Ca}_{10}\text{Al}_4\text{O}_{30})(\text{SO}_3)_5 + 40\text{H}_2\text{O}$. This formula suits not only the analysis of the Arizona mineral almost exactly, but also that of the Ettringen variety described by Lehmann, at least as well as the formula given by him. The analytical results were as follows.

	CaO.	Al ₂ O ₃ .	SO ₃ .	H ₂ O.
I	27·27	7·76	19·15	45·82
II	26·31	9·72	18·54	45·41

I, ettringite from Ettringen; II, ettringite from Arizona.

It may, therefore, be concluded that this mineral is to be placed in a group of hydrous basic sulphates of the general formula $2\text{R}_2\text{O}_3\cdot\text{SO}_3 + n\text{H}_2\text{O}$. This group is composed of—

Glockerite.....	$2\text{Fe}_2\text{O}_3\cdot\text{SO}_3 + 6\text{H}_2\text{O}$
Felsöbanyite.....	$2\text{Al}_2\text{O}_3\cdot\text{SO}_3 + 10\text{H}_2\text{O}$
Paraluminites.....	$2\text{Al}_2\text{O}_3\cdot\text{SO}_3 + 5\text{H}_2\text{O}$
Ettringite. { Arizona....	$2[\text{H}_{12}\text{CaAl}_3\text{O}_9]\text{SO}_3 + 8\text{H}_2\text{O}$
Ettringite. { Ettringen..	$2[\text{H}_2\text{CaAl}_3\text{O}_9]\text{SO}_3 + 8\text{H}_2\text{O}$

B. H. B.

Formation of Natural Aluminium and Iron Phosphates. By A. GAUTIER (*Compt. rend.*, **116**, 1491—1496).—Minervite, $\text{Al}_2(\text{PO}_4)_2 + 7\text{H}_2\text{O}$ (this vol., ii, 419), is formed by the action of ammonium phosphate, derived from a bed of guano, on an underlying layer of hydrargilite, and the aluminium phosphates in the guano islands Alta Vala, Redonda, and Commandeur have been formed in the same way. Minervite can, in fact, be obtained artificially by allowing a mixture of gelatinous aluminium hydroxide and a solution of twice its weight of ordinary ammonium phosphate to evaporate to dryness at 30°, washing in water, dissolving in hydrochloric acid, and precipitating in the cold with an excess of sodium acetate. It separates in small, short prisms and in triangular lamellæ.

Clay is slightly attacked by ammonium phosphate at about 85°, but calcium hydrogen phosphate seems to be without action on it. Similar changes take place in soils, and minute quantities of aluminium phosphate can be extracted from some soils by means of dilute solutions of alkalis.

Aluminium phosphate is slightly soluble in an ammoniacal solution of ammonium phosphate, and still more soluble in an ammoniacal solution of ammonium lactate. The latter is a product of bacteroidal

fermentation, and the fact that aluminium phosphate is soluble in the products of the fermentation of manures and soils probably has great influence on the assimilation of this compound by plants.

In contact with ferrous carbonate in fine powder, or in solution in water containing carbonic anhydride, ammonium phosphate very slowly produces ferrous phosphate. If the two substances are heated at 83° for a long time, the phosphate $\text{Fe}_3(\text{PO}_4)_2 + 6\text{H}_2\text{O}$ is formed in microscopic, acicular crystals, the composition of which differs but slightly from that of the purest varieties of vivianite, $\text{Fe}_3(\text{PO}_4)_2 + 8\text{H}_2\text{O}$.

The putrefactive decay of fish, molluscs, &c., results in the production of ammonia, together with hydrogen sulphide and hydrogen phosphide. In the case of the more stable parts, such as bone, chitinous envelopes, hair, &c., these changes, although slow, continue for a long time. For months, and even years, the change proceeds, and the substances remain distinctly alkaline. When water containing calcium and iron carbonates, calcium phosphate, &c., comes into contact with the decaying substances, precipitation takes place. Ferrous sulphide is one of the products, and by the subsequent action of hydrogen sulphide and air it becomes converted into pyrites, thus, $\text{FeS} + \text{SH}_2 + \text{O} = \text{FeS}_2 + \text{H}_2\text{O}$. Pyrites may also be formed directly by the action of hydrogen sulphide on ferrous carbonate in presence of oxygen, thus, $\text{FeCO}_3 + 2\text{SH}_2 + \text{O} = \text{FeS}_2 + 2\text{H}_2\text{O} + \text{CO}_2$. When once pyrites has been formed, it remains, by reason of its insolubility, and forms a nucleus for the deposition of a further quantity. Any calcium or aluminium phosphate, calcium or iron carbonates, &c., which may have been deposited in the decaying substance, may possibly be removed again by the solvent action of water charged with carbonic anhydride and with salts, other substances taking their place. There will, however, always be a tendency towards the accumulation of the less soluble of the substances deposited. Where, for instance, the fossil is subjected to the prolonged action of water, it may be that only silica will be left.

C. H. B.

Kehoeite, a New Phosphate from Dakota. By W. P. HEADDEN (*Amer. J. Sci.*, 46, 22—25). This mineral forms seams and bunches in an argentiferous galena carrying zinc blende and iron pyrites, at the Merritt mine, near Galena, South Dakota. Analysis gives results corresponding with the formula $\text{R}_3\text{P}_2\text{O}_8 + 2\text{Al}_2(\text{OH})_6 + 21\text{H}_2\text{O}$, in which $\text{R} = \text{Zn}_3 + \text{Ca}_4$. The mineral is named after the gentleman who first observed its occurrence.

B. H. B.

Xenotime from El Paso Co., Colorado. By S. L. PENFIELD (*Amer. J. Sci.*, 45, 398—399).—The occurrence of this mineral from the tysonite and bastnaesite locality of El Paso Co. has already been noted by W. E. Hidden (*Abstr.*, 1885, 878). An analysis of 0.2 gram of a second crystal gave the following results.

P_2O_5 .	$(\text{YtEr})_2\text{O}_3$.	Ignition.	Total.
32.11	67.78	0.18	100.07

The mineral is thus a normal phosphate. Its sp. gr. is 5.106.

B. H. B.

Rose-coloured Lime- and Alumina-bearing Talc. By W. H. HOBBS (*Amer. J. Sci.*, **45**, 404—407).—The mineral described was met with in the Adam Quarry, near Canaan, Connecticut, enclosed in white crystalline dolomite. Analysis shows that the mineral is a normal talc, in which the magnesia is in part replaced by lime, and the silica by alumina. The trace of manganese observed accounts for the rose colour, which disappears when the mineral is exposed to sunlight. The analytical results were as follows.

SiO ₂ .	Al ₂ O ₃ .	MgO.	CaO.	FeO.	MnO.	H ₂ O.	Total.
61.48	3.04	25.54	4.19	0.77	trace	5.54	100.56

The mineral is shown to belong to the talc family by its chemical composition as well as by its physical and optical properties. That it is a distinct variety is shown by its high percentages of lime and alumina, by its low fusibility and easy decomposability by acids, and by its exceptional rose colour.

B. H. B.

Zunyite from Colorado. By S. L. PENFIELD (*Amer. J. Sci.*, **45**, 397—398).—This mineral was first described by W. F. Hillebrand in 1884 from the Zuñi mine, near Silverton, Colorado. It is interesting to know that a second locality for this rare mineral has been found at the Charter Oak mine, near the town of Red Mountain, about 5 miles north of the original locality. The zunyite crystals occur in a porphyrite, much altered by steam and fumerole action. Analysis gave results corresponding with the formula $[\text{Al}(\text{Cl.F.OH})_2]_6\text{Al}_2\text{Si}_3\text{O}_{12}$, the agreement between the author's and Hillebrand's analyses being very satisfactory. Zunyite also occurs at the same mine in a pulverulent form resembling kaolin.

B. H. B.

Cookeite from Paris and Hebron, Maine. By S. L. PENFIELD (*Amer. J. Sci.*, **45**, 393—396).—Excellent specimens of the mineral cookeite, first described by G. J. Brush in 1866, have been obtained from Paris and Hebron. Cookeite is related to the chlorites and micas, having a distinct basal cleavage, and crystallising, like them, in the monoclinic system. Analysis gave results corresponding with the formula $\text{H}_{12}\text{Li}_2\text{Al}_6\text{Si}_4\text{O}_{24}$, or simplified to that of a basic metasilicate, $\text{Li}[\text{Al}(\text{OH}_2)]_2\text{Si}_2\text{O}_6$. The sp. gr. of the mineral is 2.67.

B. H. B.

Sodalite-syenite from Montana. By W. LINDGREN (*Amer. J. Sci.*, **45**, 286—297).—The author describes a series of specimens, in the United States National Museum, collected in the northern part of Montana. Descriptions and analyses are given of the following rocks: (1) Porphyrites and quartz-porphyrites from the Moccasin Mountains. They are intrusive holocrystalline rocks of post-Cretaceous age, and consist of quartz, orthoclase, soda-lime, feldspar, and hornblende. (2) Porphyritic, dark-coloured post-Cretaceous dyke rocks from the Bear Paw Mountains. They consist of augite, olivine, biotite, and triclinic feldspar, and have a general resemblance to the lamprophyric dyke rocks of Rosenbusch. (3) A post-Cretaceous so talite-syenite from Square Butte. This rock consists of hornblende, orthoclase, albite, sodalite (8 per cent.), and analcime. No nepheline

is found; but the interstitial analcime, of which there is 3 per cent., might possibly have been derived from that mineral. B. H. B.

Basic Dyke thought to contain Leucite. By J. F. KEMP (*Amer. J. Sci.*, **45**, 298—305).—In 1888 the author examined the elæolite-syenite of Beemerville, New Jersey. Since the paper describing his investigations was published, several descriptions have appeared of elæolite-syenite districts elsewhere, and in particular of the basic rocks associated with them, so that basic dykes are now recognised as invariable attendants on this form of plutonic rock. The author now describes a basic dyke, near Hamburg, not far from Beemerville, in New Jersey. The spheroidal inclusions offer the point of chief interest, as they have been thought to indicate leucite. Analysis shows that they are practically analcime. Assuming a change from leucite, it is necessary to account for a large accession of soda, and as regards the corresponding alteration from nepheline, a much smaller accession of potash. Although it is impossible to settle the question without the discovery of perfectly fresh material, either of nepheline or of leucite, in the spheroids, the analytical results rather favour original nepheline than original leucite.

B. H. B.

Volcanic Rocks from Gough's Island, South Atlantic. By L. V. PIRSSON (*Amer. J. Sci.*, **45**, 380—384).—These rocks were gathered as beech pebbles from the shore of Gough's Island, by the captain of a whaling vessel. Nothing has been published on the geology of this remote region. All the pebbles represent very fresh volcanic rocks which may be referred to trachytes or to basalts. Basalt is represented by two varieties, one of which is a rock of dark-grey colour thickly dotted with black augite, yellow olivine, and white feldspar. The second type is of a dark greyish-brown colour, exhibiting in thin sections iron ore, apatite, olivine, augite, and feldspars. It contains 49·55 per cent. of silica, and its sp. gr. is 2·643. Trachyte is represented by trachytic tuffs and obsidian. The latter gave on analysis 61·22 per cent. of silica, 1·88 of lime, and 0·44 of magnesia, whilst the percentage of soda was 6·49 and that of potash 5·93. The glass, therefore, is to be referred to trachyte, perhaps of the phonolithoid type. The analyses of these rocks are of interest in establishing the recent volcanic nature of this solitary island.

B. H. B.

Physiological Chemistry.

Nutritive Value of Albumoses. By H. HILDEBRANDT (*Zeit. physiol. Chem.*, **18**, 180—192).—Careful experiments on metabolic exchanges when albumoses are administered, given with full details, confirm the already well known fact that these substances have a high nutritive value.

W. D. H.

Nutritive Value of Proteïds. By E. KRAUSS (*Zeit. physiol. Chem.*, 18, 167—179).—In considering the metabolic value of proteïd food, it is not merely enough to put down the intake and output of nitrogen. A third factor is the amount of nitrogenous substance which undergoes putrefactive change in the intestine forming indole, &c., which, so far as the economy is concerned, is a waste. The amount of this waste can be estimated by the indican of the urine, or by the estimation of the ethereal hydrogen sulphates in the same secretion. This has recently been insisted on by Winternitz (Abstr., 1892, 1116), who made his experiments with milk, and attributes to lactose a power of lessening putrefactive change. Hirschler (Abstr., 1886, 729) regards carbohydrates as valuable antiseptics in the organism. The present experiments, performed with meat and with meat and bread diets, fully confirm this view.

W. D. H.

Proteïd in Diet. By F. HIRSCHFELD (*Chem. Centr.*, 1893, i, 790—791; from *Berl. klin. Woch.*, 30, 324—329).—Attention is called to former work (Abstr., 1889, 174) in which it is shown that less proteïd is compatible with health than was formerly supposed; and to the importance of this fact in the construction of dietaries. It is further pointed out that merely chemical analysis of a food does not form a criterion of its nutritive value. Other factors, such as weight, volume, and digestibility, must be taken into account.

W. D. H.

Influence of Tea and Coffee on Artificial Digestion. By C. SCHULTZ-SCHULTZENSTEIN (*Zeit. physiol. Chem.*, 18, 131—132).—The few experiments given show that infusions of tea and coffee, when mixed with an artificial gastric digestion in amounts approximately equal to that which would occur in the stomach after a meal accompanied by tea or coffee, impede digestion. The amount digested without such addition being 94 per cent., that in the specimens mixed with tea and coffee varied from 61 to 68 per cent.

W. D. H.

Occurrence of Hydrochloric acid in the Stomach. By F. MARTIUS (*Chem. Centr.*, 1893, i, 856).—Hydrochloric acid is rapidly secreted by the stomach, and five minutes after food has been taken it is already quantitatively detectable. Unless acids have been present in the food, the total acidity of the stomach may be taken as due to hydrochloric acid. But the acid forms a compound with the albumin of the food and so becomes indifferent towards vegetable colours.

Organic acids, and lactic acid in particular, are only secreted in amount sufficient to affect the acidity of the stomach under pathological conditions.

L. DE K.

Gases of Blood during Anæsthesia. By T. OLIVER and F. C. GARRETT (*Brit. Med. J.*, 1893, ii, 683—684).—A preliminary note on the gases of the blood during anæsthesia with chloroform, ether, methylenic dichloride, and nitrous oxide, the experiments being performed on dogs and rabbits; the most striking fact noted was a remarkable rise in the percentage of nitrogen in the blood.

W. D. H.

Chlorosis. By E. L. JONES (*Brit. Med. J.*, 1893, ii, 670—672).—From the study of the specific gravity of the blood and serum at various ages in the two sexes, the theory is advanced that chlorosis is an exaggeration of what always occurs in women at puberty, a fall in hæmoglobin and specific gravity. In the male, the opposite takes place, and they do not suffer from the disease. The connection between chlorosis and gastro-intestinal congestion is also pointed out, but the relationship is not explained.
W. D. H.

Intravascular Coagulation. By W. D. HALLIBURTON and T. G. BRODIE (*Brit. Med. J.*, 1893, ii, 682).—Analysis has shown that the proteid obtainable from various cellular organs by admixture with sodium chloride, in a method already described (this vol., ii, 133), is a nucleo-albumin, and thus resembles Wooldridge's tissue fibrinogen. The physiological effect of the two substances is also identical, leading to intravascular clotting, chiefly in the venous, but also sometimes on the arterial side of the circulation. Death occurs from stoppage of the respiration, and the fact that severance of the vagi makes no difference in the experimental result points to the cause of death in the respiratory centre. The toxic material may be conveniently dried in a vacuum at a low temperature, and dissolved for use in dilute sodium carbonate solution. Such solutions are clear, somewhat viscous, and free from lecithin. Even when kept antiseptic with thymol, they lose their power after some days, and a curious change noticed was that after some weeks they became pink, and subsequently red. The spectroscope reveals no bands.

The use of nucleo-albumin to produce clotting in hæmorrhages, or aneurisms, cannot be recommended, as the substance is so deadly. Sir Joseph Fayrer (see next abstract) and others have pointed out that intravascular coagulation is by no means an infrequent cause of death, and it can hardly be doubted that the poisonous substance here also is a nucleo-albumin.
W. D. H.

Cardiac and Pulmonary Thrombosis. By J. FAYRER (*Brit. Med. J.*, 1893, ii, 682—683).—Clinical details of two cases are given.

W. D. H.

Glycogen in Blood and Pus. By HUPPERT (*Zeit. physiol. Chem.*, 18, 144—166; compare this vol., ii, 176).—Full details are given of the experiments on which the author rests his conclusions. The leucocytes in the blood are probably the source of the glycogen found.

W. D. H.

Influence of Fever on Hepatic Glycogen. By D. NOËL PATON (*Brit. Med. J.*, 1893, ii, 682).—Since it is the disintegration of proteids, and not of fats and carbohydrates, which characterises the metabolism of fever, it is important to investigate the effect of that condition on the glycogen of the liver. In the experiments, pairs of young rabbits were kept on the same diet, and weighed daily for considerable periods, thus rendering the hepatic glycogen fairly uniform. By diminishing the heat elimination by placing one of the pair in a hot chamber, the body temperature rose, and on killing it the glycogen was markedly diminished, as compared with that in the other

rabbit. At the same time, the reducing substances of the blood and liver were increased, probably indicating sugar formed from the glycogen. Pyrexia, produced by toxic products (yeast culture), led to corresponding results. The effect may be partly explained also by diminished formation of glycogen. W. D. H.

The Work of the Kidney. By W. H. THOMPSON (*Brit. Med. J.*, 1893, ii, 681).—The experiments were made on dogs, and the urine collected by cannulae in the ureters. 1.5 to 2 milligrams of atropine, and in other cases 3 to 4 milligrams of morphine, per kilo. of body weight were given intravenously. The results were, that the urine was diminished, and urea also was diminished; the nitrogen, other than that in urea, was increased. These results could not be explained as the result of interference with blood pressure, but taken with the fact that heat is produced in the kidney during its performance of work, tends to the belief that some of the urea is formed in the kidney itself out of one or more of the other nitrogenous compounds, and that this process of true secretion is lessened by the drugs which produce similar effects in other glands. W. D. H.

Carbohydrates of Normal Urine. By K. BAISCH (*Zeit. physiol. Chem.*, 18, 193—206).—The investigations of the older chemists showed that the presence of a reducing substance, presumably sugar, was constant in normal urine. It was not, however, until Baumann's benzoic chloride method was introduced that it became possible to isolate this substance and to study its properties, and even now the matter is far from settled, Wedenski having shown that the carbohydrates are probably two in number, and that the benzoyl compound contains small quantities of nitrogen (*Abstr.*, 1889, 293). The present research relates mainly to the preparation and properties of the benzoyl compound. Future papers are promised on the varieties of carbohydrate which can be obtained from it. It is, however, briefly stated that the properties of one of these corresponds closely to those of dextrose.

The best proportions of reagents to use are 40 c.c. of benzoic chloride, 400 c.c. of sodium hydroxide, and a litre of urine. Other proportions give a smaller yield with a larger amount of ash; the ash consists chiefly of magnesium phosphate, which can be removed by means of dilute hydrochloric acid. But in all cases there is from 1 to 2 per cent. of nitrogen. Similar results followed if the urine had been previously treated with normal or basic lead acetate. The melting point varied in different preparations from 95° to 130°; the carbon from 66.5 to 67.7, the hydrogen from 5.15 to 5.57.

W. D. H.

Episarkine. By G. SALOMON (*Zeit. physiol. Chem.*, 18, 207—212). Balke (this vol., i, 536) has recently described under this name a new xanthine-like compound in the urine. It appears to be identical with a substance of hitherto doubtful nature, described by the author at various times, in the urine of the pig and ox, and in the urine of leucæmic patients. Further details are promised.

By the solubilities of their silver compounds in hot nitric acid, the

xanthine-like substances of the urine may be divided into the hypoxanthine fraction, including hypoxanthine, guanine, carnine, adenine, and episarkine, and the xanthine fraction, which includes xanthine, paraxanthine, and heteroxanthine.

W. D. H.

Diabetic Coma. By V. HARLEY (*Brit. Med. J.*, 1893, ii, 666—669).—Coma can be produced in dogs by the introduction of sugar into the circulation, the ureters being tied. The comatose stage is preceded by a convulsive one. This is not simply due to the ligature of the ureters, nor is it due to the sugar, which diminishes in the blood as the symptoms appear. It is due to toxic substances produced from the sugar. Alcohol and acetone were found, and these may be partly the cause of the diminished oxidation which experiments on the gaseous interchanges show. Coma is, however, principally due to acid products which combine with the carbonates and ammonia of the blood, thus hindering that fluid from carrying carbonic anhydride to the lungs for elimination. There is at the same time a diminution in the oxygen absorbed. β -Hydroxybutyric acid is not formed.

W. D. H.

Amount of Lecithin in Butter. By E. WRAPPELMAYER (*Landw. Versuchs-Stat.*, 42, 437—438).—The ash from 100 grams of butter yielded 0.04512 gram of phosphoric acid, whilst margarin gave only 0.0160 gram. Analyses made with filtered fat showed that the ash of margarin treated in this manner contained practically no phosphoric acid, whilst the ash of butter was found to contain much reduced and very variable quantities. The average amount of lecithin calculated on the total phosphoric acid now found was 0.017 per cent. (Beilstein, 2 Ed., 1, 334, gives 0.15—0.17 per cent.). The results of analyses of seven samples is given in a table, which shows also the melting and solidifying points of the butters, and the amounts of volatile fatty acids.

N. H. M.

Influence of Chloral Hydrate and Amylene Hydrate on Metabolism. By E. HARNACK and J. REMERTZ (*Chem. Centr.*, 1893, i, 841—842; from *Fortsch. d. Med.*, 11, 265—270).—The experiments were tried on dogs. The sulphur in dog's urine is in four conditions, and not in three, as in human urine. These are A, as ordinary sulphates; B as ethereal hydrogen sulphates; C, as thiosulphates (absent in human urine); and D, as organic sulphur compounds. Chloral hydrate increases the output of sulphur by 18 per cent.; this is due to increase of B and D. Amylene hydrate lessens the total output of sulphur, as it depresses the oxidation processes in the organism. Chloral hydrate diminishes the excretion of urea during the first two days of its administration, and increases it subsequently. The total nitrogen runs the same course, but the effect is not merely due to urea, but also to organic compounds which contain sulphur in addition. This is due to increased metabolism of tissue proteid, rather than to an increase of oxidation processes. The chloral itself leads to an increase of urinary chlorides. Amylene hydrate lessens the output of nitrogen and urea. Both hypnotics lessen oxidation, and

lower the body temperature. This action appears to be independent of their narcotic and paralytic effects, which are due rather to the alkyl than to the halogen.

W. D. H.

Physiological Action of Pyridine and Naphthalene Derivatives. By R. COHN (*Zeit. physiol. Chem.*, **18**, 112—130).—His (*Arch. exp. Path. Pharm.*, **22**) found that pyridine leaves the body in the urine as methylpyridylammonium hydroxide, $C_5NH_5Me \cdot OH$; as this investigation was made previous to the publication of Ladenburg's (*Annalen*, **247**, 1) method of preparing pure pyridine, and as the result is unique in animal chemistry, it was thought advisable to repeat the experiments. The results obtained by His were completely confirmed by those of the present research. Attempts to obtain pyridine aldehyde by Ladenburg's method from α -picoline having failed, the action of α -picoline itself on the body was investigated; this substance was found to leave the body as a glycocine compound of α -pyridinecarboxylic acid, to which the name α -pyridinuric acid is given.

Nencki states that naphthalenecarboxylic acid leaves the body in the urine unchanged (*Arch. exp. Path. Pharm.*, **30**, 302); this was put to the test. It was found that in rabbits the α -acid is excreted unchanged, but the β -acid leaves the body as the glycocine compound, β -naphthuric acid. In dogs, the β -acid is excreted unchanged, while the α -acid leaves the body as α -naphthuric acid.

W. D. H.

A complete Process of Reduction occurring in the Animal Tissues. By R. COHN (*Zeit. physiol. Chem.*, **18**, 133—136).—The author has previously shown (*Abstr.*, 1892, 1504) that in rabbits metanitrobenzaldehyde leaves the body in the urine as acetylamido-benzoic acid. This involves three changes: 1st, an oxidation of the aldehyde group to a carboxyl group; 2nd, a reduction of the nitro-group to an amido-group; and, 3rd, a synthesis with acetic acid, water being eliminated. In the dog, this does not occur, and the shortness of its alimentary canal was regarded as the probable explanation of the difference. But the present experiments show that this cannot be correct, as the reduction occurs in the tissues after subcutaneous injection; indeed, more of the reduction product is then obtained in the urine than when the drug is given in the usual way.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Nitrification. By E. GODLEWSKI (*Forsch. a. d. Gebiete d. Agrik. physik.*, **16**, 240—242; from *Anzeiger d. Akad. d. Wissens. Krakau*, 1892).—According to Winogradsky, both the nitrite and the nitrate organisms have the power of vegetating in solutions absolutely free from organic matter, as, for instance, a solution containing ammonium

sulphate and potassium phosphate, with addition of basic magnesium carbonate, and he concludes that the organisms derive their carbon from the magnesium carbonate. This view was opposed by Elfving (*Forsch. Geb. Agrik. phys.*, **14**, 304), who considered it more probable that the organisms derived their carbon from volatile compounds absorbed from the air. The following experiment was made by the author.

Four Erlenmeyer flasks, each containing water (100 c.c.), ammonium sulphate (0.05 gram), potassium phosphate (0.1 gram), and magnesium carbonate (1 gram), and seeded with 1 drop of a nitrifying organism cultivation, were kept under the following conditions. No. 1 was closed with cotton wool; Nos. 2, 3, and 4 were placed on glass dishes and covered with bell jars, which were closed below with potash, sulphuric acid, and a permanganate solution respectively. In the flask exposed to air, nitrification was vigorous; in those kept over sulphuric acid and over permanganate, it was also vigorous, but somewhat slower; whilst in the flask kept over potash, there was no nitrification at all. The experiment was repeated with the same result. It is concluded that the organisms derived their carbon from the carbonic anhydride of the air or of the double carbonate.

In a second series of experiments, in which known amounts of ordinary air, or air containing large amounts of carbonic anhydride, were employed, it was found that the carbonic anhydride actually did nourish the micro-organisms. The nitrogen of the air increased, showing that in the process of nitrification a portion of the nitrogen of the ammonia is liberated.

N. H. M.

Changes in Mouldy Bread. By A. HEBEBRAND (*Landw. Versuchs-Stat.*, **32**, 421—427).—Samples of rye bread were infected from mouldy bread, and kept for periods of 7 and 14 days, similar samples being at once dried for analysis. The mould was chiefly *Penicillium glaucum* and *Mucor mucedo*. The results showed that there was a considerable loss of substance under the influence of mould, mainly owing to the conversion of the carbohydrates into carbonic anhydride and water. The fat and crude fibre increased in amount, whilst, although there was only a slight loss of proteid matter, the loss of carbohydrates caused the percentage of proteids to be much higher in the dry substance of the mouldy bread. The decomposition of proteids caused an increase in the amount of amides. In a subsequent experiment, the bread (47.65 grams) was first sterilised, and then seeded with a pure cultivation of *Penicillium glaucum*. The carbonic anhydride evolved was determined, and it was found that it amounted to about 21.5 milligrams per hour. At the conclusion of the experiment, the flask containing the bread was heated in a glycerol bath, and the distillate collected. This had an odour of fresh cider refuse, and was strongly acid; it contained no alcohol. The bread had lost 18.69 per cent. of its weight of dry substance. The following numbers show the percentage composition (1) of the dried fresh bread and (2) of the dried mouldy bread.

	Crude protein.	Pure protein.	Soluble protein.	Maltose.	Dextrin.	Starch.	Fat.	Pure ash.	Crude fibre.
1.	11.94	(11.67)	(1.92)	1.54	8.02	76.75	0.26	1.44	0.05
2.	17.13	(14.92)	(5.15)	0.50	11.86	63.52	2.11	2.41	2.47

There were thus gains of fat and crude fibre (0.71 and 0.98 per cent. respectively), and losses of starch (20.03), maltose (0.72), and protein (0.11 per cent.). No ammonia could be detected. The number given for starch in the mouldy bread was found by difference, and is slightly high, as small amounts of other substances were present. Among these, only volatile acids, oxalic acid, and mannitol could be detected, owing to the smallness of the amounts.

N. H. M.

Composition of the Ripe Husks of Capsicum. By B. v. BIRTÓ (*Landw. Versuchs-Stat.*, **42**, 369—379).—The first analysis of capsicum seem to be that made by Buchholz (König, *Die menschl. Nahrungs- u. Genussmittel*, 2 Aufl., **1**, 148), whilst a more thorough examination of the fruit was made by Braconnot (*Ann. Chim. Phys.*, **21**, 124), who obtained capsicin, a soft, non-crystalline compound with a pungent taste, and from this capsicum-red. Witting (*Rep. Pharm.*, **13**, 366) and Tresh (*Pharm. Centr.*, **17**, 427) maintain that the active constituent is a crystalline substance termed capsäicin. Pabst (*Arch. Pharm.*, **23**, 108) found a trace of an alkaloid; he considers capsäicin to be an amorphous acid; and he detected considerable amounts of free oleic, stearic, and palmitic acids in the fruit. He concludes that the red colour of the fruit is probably carotin (compare also Felletár, *J. Pharm.*, 1868, 70; Fleischer, *Arch. exp. Path.*, **9**, 117; and Strohmer, *Chem. Centr.*, 1886, 577).

The ripe fruit examined by the author was well developed, and of a scarlet colour. The amounts of the different parts of the fruit vary considerably, owing to the varying amount of seed.

The whole fruit (1) was found to contain 90.25 per cent. of dry matter, (2) the fruit husk 85.86 per cent., (3) the seed 90.49, and (4) the placenta 87.34 per cent. The dry matter has the following composition.

	Ash.	Ether extract.	Nitrogenous matter.	Non-nitro- genous extract.	Crude fibre.	Nitrogen.
1.	6.76	10.69	19.77	39.82	22.95	3.16
2.	5.66	5.14	14.31	49.07	25.83	2.29
3.	4.35	27.95	17.22	33.07	17.36	2.93
4.	11.03	7.07	28.54	39.88	13.48	4.57

	Nitrogen as ammonia.	Nitrogen. as amides.	Proteid nitrogen.
1.	0.217	0.093	2.321
2.	0.195	0.130	1.792
3.	0.061	0.061	2.938
4.	0.240	0.280	2.403

The following ash analyses are given of (1) the whole fruit, (2) the husks, and (3) the seed.

	K ₂ O.	Na ₂ O.	MgO.	CaO.	Al ₂ O ₃ .	Fe ₂ O ₃ .
1.	55.60	4.42	6.22	4.80	trace	1.44
2.	52.47	13.16	5.04	5.08	0.22	1.69
3.	40.12	2.50	10.43	3.46	—	0.81
	SiO ₂ .	Cl.	SO ₃ .	P ₂ O ₅ .		
1.	2.04	3.88	6.44	16.82		
2.	1.90	1.44	4.58	14.59		
3.	1.74	2.65	4.97	33.95		

As regards the manufactured products, the ordinary kinds are made by grinding the whole fruit, the stem being frequently included; they have a pale brick-red colour. The best preparations are made with the husks and seeds only. To detect adulteration, microscopic examination is necessary, as well as estimation of the ash. The pure ash is usually white or slightly greenish, and dissolves almost entirely in dilute acids. Tables are given showing the results of analyses of manufactured products.

N. H. M.

Lathyrus sylvestris. By E. KINCH (*Agrl. Students' Gazette*, New Series, 6, 108—109).—This leguminous plant has been introduced as a cultivated fodder plant suitable for poor soils, under the name of Wagner's flat pea or wood vetchling. The plot of this plant cultivated at the Royal Agricultural College, Cirencester, yielded 30 cwt. of hay per acre on May 30, 1893, and a second crop on August 4 of the same year. 1000 parts of the green stuff gave 184 parts of air-dried hay which contained 16.82 per cent. of moisture. The following analyses were made.

	Green stuff.	Dry matter of hay.
Water	84.70	—
Ash	0.86	5.62
Fibre	4.43	28.97
Ether extract	0.65	4.25
Nitrogenous matter	5.41	35.33
Soluble carbohydrates	3.95	25.83
	<hr/>	<hr/>
	100.00	100.00
True proteids	3.51	22.86

It will be seen that the nitrogen content of the hay is greater than that of peas or beans, but a much larger proportion (35 per cent.) is of an amide character. It contains twice as much nitrogen as lucerne hay, and about three times as much as meadow hay. The ether extract contained a good deal of chlorophyll.

A. G. B.

Analysis of Tobacco cured by the Leaf-cure on Wire, and by the Stalk Process. By F. B. CARPENTER (*Exper. Stat. Record*, 4, 819—821; from *N. Carolina Stat. Bull.*, No. 90A, 1893).—The two methods of curing have been already described (*Exper. Stat. Record*, 4, 32—35). In the leaf-cure on wire, the leaves are stripped from the stalk at three different periods and strung on wires; whilst in the

stalk process the leaves are left on the stalks and kept in an ordinary barn. Owing to the manner and time of harvesting, the chemical composition of the products of the two processes varies somewhat. In the leaf-cure process, the priming of the lower leaves causes increased growth, and an increase in the percentage of proteïds and nicotine. But the loss in quality caused by this transformation is more than compensated by the gain in weight.

The results of analyses made with plants of various age showed that nitrates are almost entirely confined to the stalk and stems in the younger growth of the plant, whilst the other nitrogen compounds are more abundant in the leaves.

N. H. M.

Greater Assimilability of the Nitrogen of recently formed Nitrates. By P. PICHARD (*Compt. rend.*, 117, 125—127).—The results of all the author's experiments indicate that nitric nitrogen is most efficacious and assimilable when recently formed or when it has migrated from one base to another, especially when the new base is potash. The use of sodium nitrate as a manure in preference to the potassium salt is not only to be recommended on account of its cheapness, but also because of its conversion into the potassium salt in a soil containing potash. Again, the repeated application of small quantities of sodium nitrate has the advantage of continually furnishing the plant with newly formed potassium nitrate, besides the obvious advantage of diminished loss in drainage. It is probable that the nitrates observed by Berthelot to be formed within the plant tissues are still more assimilable than the nitrates of the soil. Vegetation will be more greatly benefited by the old methods of cultivation, which tended to induce increased nitrification in soil, than by the direct application of nitrates.

N. H. M.

Combined Nitrogen in Rain. By A. PETERMANN and J. GRAFTIAN (*Bull. Stat. agron. Gembloux*, 1893, No. 52, 5—26).—Rain was collected by means of a nicked copper collector (82 cm. in diameter), in a large glass vessel; mercuric chloride was added to prevent change. Determinations of ammonia and nitrates were made from January, 1889, to December, 1891, whenever there was sufficient water for analysis, the ammonia being determined with Nessler solution after distillation with a little potash, and the nitrates after reduction to ammonia by the zinc-copper couple. The average rainfall was 692 mm. (= 27.14 in.) per annum and contained: ammoniacal nitrogen, 1.14 per million; nitric nitrogen, 0.35 per million; total, 1.49 per million. Calculated in kilos. per hectare per annum, the amounts are as follows: nitrogen as ammonia, 7.92 kilos. (or 7.07 lbs. per acre); nitrogen as nitrates, 2.39 kilos. (or 2.13 lbs. per acre); total, 10.31 kilos. (or 9.20 lbs. per acre). This total is less than the average found at Montsouris (14.28 kilos.) and at the Italian and German stations, but higher than that obtained at Rothamsted.*

* 7.36 kilos. per hectare (= 6.57 lbs. per acre) is given as the average annual amount at Rothamsted. The authors give no indication as to where they obtained this figure, which is nearly, but not quite, the same as was obtained at Rothamsted in the years 1853-56. More recent results showed that the amounts of nitrates and

The relation of ammoniacal to nitric nitrogen is 76 : 24, which is very nearly the same as at Rothamsted (75 : 25) and at Montsouris and the German and Italian stations (73 : 27). The February rain was found to be the richest in nitrogen, that of July the poorest. The greatest rainfall was in July, the lowest in February; whilst as regards the total amounts of nitrogen in the rain, the highest was observed in August, the lowest in February. Tables are given containing the results of each of the 142 analyses made during the three years.

Separate analyses were made of hoar-frost and snow, collected in or near the grounds of the Institute. The hoar-frost contained an average amount of combined nitrogen = 7.52 per million; the snow, 7.40 per million.
N. H. M.

Soluble Phosphoric acid in Superphosphate. By J. STOKLASA (*Landw. Versuchs-Stat.*, 42, 439—457; compare *Abstr.*, 1891, 880).—Calcium carbonate and calcium phosphate, $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, were well mixed in molecular proportion, treated with 500 c.c. of water, and the whole evaporated to a small bulk. It was then diluted with water, filtered, washed, and dried over sulphuric acid until the weight was constant. The residue was pure calcium phosphate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. When twice the amount of calcium carbonate was employed, pure tricalcium phosphate was obtained (compare Weilandt, *Abstr.*, 1887, 995). This reaction, showing the production of the less soluble triphosphate, is one of importance for the absorption in soil. Thus, soil, containing only 0.4 per cent. of calcium carbonate, will contain 6000 kilos. per hectare to the depth of 10 cm.; taking the maximum amount of soluble phosphate applied to the soil (100 kilos. per hectare), there will be 33 parts of calcium carbonate to 1 of monocalcium phosphate. The results of experiments with plants have shown the better effects of diphosphates as compared with the less soluble triphosphate. Chalky soils manured with monocalcium phosphate never gave as good crops (turnips, barley, and peas) as were obtained when orthophosphoric acid was employed. Inasmuch as the exact composition of superphosphates has not been ascertained, the author considers that the experiments hitherto made are incomplete and of less use than is usually supposed.

A considerable number of experiments are described in which calcium phosphate, $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, was submitted to the action of pure calcium carbonate in different forms, under various conditions. It was found that a mixture of the dry salts gradually changed, the amount of soluble phosphate falling from 55.4 per cent. after two hours to 21.02 per cent. after 360 days. Calcareous sandstone kept in a solution of the phosphate became covered with a layer of tricalcium phosphate. Experiments in which calcite was employed showed that more triphosphate is formed with strong than with weaker solutions.

ammonia were a good deal less than was supposed, and the total nitrogen (excluding nitrogenous organic matter) is now shown to be about 3.5 lbs. per acre per annum (compare *Jour. Roy. Agr. Soc.* [2], 17, 241, and 19, 313; *Trans. Chem. Soc.*, 1889, 537).
N. H. M.

Zinc cylinders of different sizes were filled with sand containing 20 per cent. of pure calcium carbonate. Pure monocalcium phosphate, $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (7 grams), was mixed with the top 5 cm. of the sand, and water poured on to the amount of 2 litres in 10 days. At the end of this time, each cylinder had another 2 litres of water. The drainage, which was quite clear, did not contain a trace of free phosphoric acid. Nearly the whole of the phosphates remained in the sand in an insoluble form.

In order to ascertain the effect of water on calcium phosphate, 1 kilo. of pure sand containing 19 per cent. of water was superficially treated with methyl-orange, and a gram of phosphate distributed over the surface. The pieces of phosphate immediately became red. In presence of 2 per cent. of calcium carbonate, single particles became red, the acid being neutralised. When loam was used instead of sand, the decomposition was slower. The results of these and other experiments point to the conclusion that orthophosphoric acid is first liberated and that this reacts with the calcium carbonate (2 mols.), yielding tricalcium phosphate.

N. H. M.

Analytical Chemistry.

Titration of Acids by Metallic Sodium. By E. NEITZEL (*Zeit. anal. Chem.*, **32**, 422—423).—The author recommends anew Hartley's proposal (this Journal, 1873, 132) to employ weighed quantities of metallic sodium for the titration of standard acids. He prefers to weigh the block of sodium under petroleum which has been heated above 100° and filtered. For this purpose a beaker containing petroleum is tared on the balance, and the block of sodium, cut clean from a larger mass as rapidly as possible, is at once slipped into the petroleum and weighed. Such a block, of about 0.7 gram, gains only about 0.17 milligram during the 15 seconds required for cutting it out. The sodium is then withdrawn with tongs, and without regarding the adhering petroleum, is treated with 75 c.c. of 88—94 per cent. alcohol in a flask fitted with a perforated cork and glass tube. When all is dissolved, water and the indicator are added, and the solution is ready for titration.

M. J. S.

Estimation of Chlorine in Water. By T. FAIRLEY (*Analyst*, **18**, 222).—The author confirms Young's statement (compare this vol., ii, 433) that water should be concentrated before titrating with silver nitrate and potassium chromate. But even then the result will not be absolutely trustworthy if the water contains traces of alkali silicate.

L. DE K.

Iodometric Estimation of Nitrates. By H. GRUENER (*Amer. J. Sci.*, **46**, 42—50).—The author describes two new processes which, under special conditions, may be found useful.

1. *Reduction by means of Phosphoric acid and Potassium Iodide.*—A quantity of nitrate, not exceeding 0.05 gram of potassium nitrate, is introduced into a retort with 10 times its weight of potassium iodide and 17–20 c.c. of phosphoric acid (sp. gr. 1.43). The neck of the retort passes into a receiver containing a known amount of decinormal arsenious oxide, containing an excess of sodium hydrogen carbonate. For additional safety, a simple trap containing water should be attached. The solution is distilled in a current of carbonic anhydride until every trace of iodine is removed. The contents of the receiver is now titrated with iodine to find the amount of unoxidised arsenious acid. This gives the measure of the iodine evolved, and, consequently, of the nitrate present, the reaction in the retort being $2\text{HNO}_3 + 6\text{HI} = 4\text{H}_2\text{O} + 2\text{NO} + 3\text{I}_2$.

2. *Reduction by means of Antimonious Chloride.*—The dry nitrate is introduced into a diminutive retort made from a pipette shaped like a "Liebig's drier," and connected by a sliding joint, covered by india-rubber, into a Kjeldahl tube used as a receiver, and so placed that carbonic anhydride, passing through the apparatus, enters from below. The nitrate is washed down with a few drops of hydrochloric acid and a definite amount of antimonious chloride is added from a burette. The receiver is charged with 0.25 gram of potassium iodide, dissolved in recently boiled water, and is joined to a trap filled with water. After passing carbonic anhydride through the apparatus for 10 minutes, the solution is heated in an oil-bath at $103\text{--}107^\circ$, and after 15 minutes heating the receiver and trap are washed out and at once titrated with sodium thiosulphate. The solution in the retort is now diluted with solution of tartaric acid, nearly neutralised with a 25 per cent. solution of sodium hydroxide, mixed with excess of sodium hydrogen carbonate, and titrated with decinormal iodine.

The difference between the trichloride left in the retort and the iodine found in the receiver is the measure of trichloride left unoxidised by the nitrate, and the difference is the measure of the nitrate present. The test analyses are fairly satisfactory.

L. DE K.

Estimation of Nitrates by Schmitt's Method. By K. WEDEMEYER (*Arch. Pharm.*, **231**, 372–376).—10 c.c. of acetic acid, 10 grams of a mixture of equal parts of finely powdered iron and zinc, and 25 c.c. of water are placed in a flask of about 1500 c.c. capacity, a funnel is placed in the neck of the flask, and into the funnel is shaken a weighed quantity (0.3–0.8 gram) of the nitrate to be estimated, which is then washed down into the flask. Heat may be applied, so long as the temperature does not exceed 80° , and the funnel and walls of the flask must be washed down from time to time. After 10 minutes, the reduction is complete, and the ammonia may be distilled off and estimated as in Kjeldahl's method. Excellent results are obtained with nitrates; with nitrites they are too low.

C. F. B.

Methods of estimating Sulphur. By L. MARCHLEWSKI (*Zeit. anal. Chem.*, **32**, 403–411; see this vol., ii, 186).—*Gröger and Treadwell's Method.*—Pyrites is heated with metallic iron until converted into ferrous sulphide. This is decomposed by hydrochloric acid

and the liberated hydrogen sulphide absorbed in an iodine solution. With pure pyrites, the method yields excellent results, but, as a technical method, it is useless, since sulphates, such as barium and lead sulphates, would be partially reduced by the iron powder, if present, and would thus produce fictitiously high results.

Sauer's Method (this Journal, 1873, 939).—Zulkowski's simplified modification of this method is as follows. A combustion tube, 60 cm., or, for pyrites, 40 cm., long, is drawn out at one end to a long, narrow tube, which is bent downwards and connected with an absorption apparatus consisting of two bulbed U-tubes and a tube containing glass wool. The absorption liquid is 30 c.c. of an alkaline hypobromite solution, made by dissolving 180 grams of potash (free from sulphates), adding 100 grams of bromine, and making up to a litre. Next to the narrowed part of the tube comes 20—25 cm. of platinised asbestos, and at a distance of 7—10 cm. from this is placed the boat containing the substance (0.4 gram of sulphur). To the further end of the tube is attached an oxygen gas holder, with a wash bottle containing water as indicator. The tube is filled with moist oxygen while heating the platinised asbestos, and then heat is gradually applied to the substance. Finally, any sulphuric acid which may have condensed in the narrow part of the tube is driven over as far as possible by heat and then washed out. The absorption liquid is then acidified, heated, and precipitated by barium chloride. When assaying pyrites, the platinised asbestos is omitted. The method gives accurate results, but is tedious; it can, of course, be used in presence of non-volatile sulphates.

The author has been unable to get satisfactory results by Föhr's method, which consists in absorbing the hydrogen sulphide by ammoniacal zinc solution, then adding ferric sulphate, and titrating the reduced ferrous salt by permanganate. Also, in common with Friedheim (Abstr., 1886, 739), he considers Klobukow's method (Abstr., 1885, 1159) as useless.

M. J. S.

Treatment of Barium Sulphate in Analysis. By J. I. PHINNEY (*Amer. J. Sci.*, 45, 468—472).—The author, having carried out a large number of experiments, concludes that the barium sulphate should preferably be collected on a Gooch's asbestos filter, so as to avoid reduction of the sulphate by the filter-paper. Alkali chlorides contaminate barium sulphate thrown down in the presence of an excess of sulphuric acid, and are not completely removed by ignition and subsequent treatment with hydrochloric acid. According to the author, the only good method for purification is either to fuse, according to Fresenius, with sodium carbonate, extract, and reprecipitate as sulphate, or to evaporate from solution in strong sulphuric acid as proposed by Mar.

L. DE K.

Influence of Nitric acid and Nitro-hydrochloric acid on the Precipitation of Barium Sulphate. By P. E. BROWNING (*Amer. J. Sci.*, 45, 399—404).—The author has proved by a series of carefully made experiments that the presence of an excess of nitric acid, or nitro-hydrochloric acid, amounting to 10 per cent. by volume of

the liquid, is not only not to be avoided in estimating barium as sulphate, but it is actually to be recommended. When precipitated from such acid solutions, the sulphate is coarsely crystalline and heavy, and less liable to carry down impurities; and even in certain special cases where there are substances which exercise a solvent action, the precipitation is made complete.

To make sure that the correctness of the results was not due to a compromise between any loss caused by the solvent action of the acids and the increase caused by the co-precipitation of alkali salts, &c., the author took the precaution of recrystallising the barium sulphate from hot concentrated sulphuric acid. It was then again washed with water.

L. DE K.

Emmerton's Process for the Estimation of Phosphorus.

By H. C. BABBITT (*Chem. Centr.*, 1893, i, 957—958; from *J. anal. Chem.*, 7, 165—168).—If the precipitation with ammonium molybdate is conducted at a temperature exceeding 25°, the precipitate may contain arsenic. The yellow precipitate contains 1.63 per cent. of phosphorus. The precipitation is complete within five minutes if a whirling apparatus is used. The reduction by means of zinc and sulphuric acid gives the compound $\text{Mo}_{12}\text{O}_{19}$; reduction by means of zinc-dust is not to be recommended, as constant results cannot be obtained.

L. DE K.

Colorimetric Analysis of Phosphorites. By A. NASTIUKOFF (*J. Russ. Chem. Soc.*, 25, 31—42).—The author has made a number of experiments on natural and artificial phosphorites, which tend to show the possibility of estimating the amount of phosphoric acid present in them by means of the bluish-grey colour produced when they are heated with insufficient access of air. A platinum crucible is two-thirds filled with finely-sifted phosphorite, and heated with the lid on in a gas flame for 10 to 15 minutes, during which time the lid is twice or thrice removed, and the contents stirred up with a platinum wire. No details are given as to how the colorimetry is carried out. The method is said only to hold within certain limits of composition, and not for all phosphorites.

J. W.

Estimation of Phosphorus in Steel. By C. B. DUDLEY and F. N. PEASE (*Chem. Centr.*, 1893, i, 957; from *J. anal. Chem.*, 7, 108—115).—1 gram of the sample is dissolved, in an Erlenmeyer flask, in 75 c.c. of nitric acid of sp. gr. 1.15; when dissolved, it is boiled for a minute and mixed with 10 c.c. of a solution of potassium permanganate, and then again boiled until manganese dioxide begins to separate. The liquid is now cleared by the cautious addition of pure ferrous sulphate, heated to 85°, and mixed with 75 c.c. of ammonium molybdate solution at 27°. After shaking for five minutes in the authors' apparatus, the precipitate is washed with solution of ammonium sulphate until the washings give no coloration with ammonium sulphide, and then dissolved in a mixture of 5 c.c. of ammonia and 25 c.c. of water. The solution is now mixed with 10 c.c. of strong sulphuric acid, diluted to 200 c.c., and filtered through a tube containing a perforated platinum crucible filled with granulated zinc. The lower end of the tube

is fitted with another perforated platinum crucible containing sand. The filtrate is now titrated with potassium permanganate. The amount of permanganate which represents 1 gram of iron equals 0.0172444 gram of phosphorus. L. DE K.

Estimation of Phosphorus in Iron in presence of Arsenic. By E. D. CAMPBELL (*Chem. Centr.*, 1893, i, 795; from *J. Anal. Chem.*, 7, 2—3).—The author estimated the phosphorus gravimetrically as ammonium phosphomolybdate. In some experiments, potassium arsenate was purposely added in order to see whether the presence of arsenic would interfere with the process. The results showed conclusively that, unless the arsenic is first removed by means of oxalic acid, serious errors will arise. L. DE K.

Estimation of Potassium. By A. VILLIERS and F. BORG (*Compt. rend.*, 116, 1524—1527).—See this vol., ii, 521.

Quantitative Separation of Cæsium. By H. L. WELLS (*Zeit. anorg. Chem.*, 4, 341—345; and *Amer. J. Sci.*, 46, 186).—See this vol., ii, 521.

A Reaction of Cupric Salts. By E. LENOBLE (*Bull. Soc. Chim.* [3], 9, 137—138).—On the addition of potassium mercuric iodide to cupric sulphate in aqueous solution, a bright red precipitate is formed, and can be freed from iodine by treatment with water. The compound appears to be *cuprous mercuric iodide*, $\text{Cu}_2\text{I}_2 \cdot 2\text{HgI}_2$; but its exact composition is probably dependent on that of the potassium mercuric iodide and on the concentration of the reagents. As a qualitative test, the reaction serves to indicate the presence of copper in solutions containing 1 part in 1000. J. B. T.

Volumetric Estimation of Arsenic and Antimony. By S. GYÖRY (*Zeit. anal. Chem.*, 32, 415—421).—Arsenious and antimonious oxides are converted into the respective pentoxides with quantitative accuracy by the action of potassium bromate, the quantities concerned agreeing with the equation $2\text{KBrO}_3 + 2\text{HCl} + 3\text{As}_2\text{O}_3 = 2\text{KCl} + 2\text{HBr} + 3\text{As}_2\text{O}_5$. The method has so far been tested only on pure sodium arsenite (Fowler's solution) and potassium antimonyl tartrate. A decinormal bromate solution is obtained by drying the salt at 110° and dissolving 2.7850 grams to 1 litre. The arsenious or antimonious solution is freely acidified with 10 per cent. hydrochloric acid, a drop of a 1 per cent. solution of methyl-orange is added, and the bromate solution is run in until the methyl-orange pink colour disappears, leaving the liquid colourless. The end reaction is extremely sharp, one-tenth of a drop of bromate sufficing to discharge the colour. M. J. S.

Estimation of Chromium in Products of the Iron Industry. By G. GIORGIS (*Gazzetta*, 23, i, 277—284).—The author has devised the following rapid and accurate method of estimating chromium in steel or other metallurgical products. The steel is dissolved in sulphuric and nitric acids, and the solution made up to 1 litre.

250 c.c. of this is then rendered just alkaline with soda, and potassium permanganate is added to the heated solution until a permanent red colour is produced; after cooling, the excess of permanganate is destroyed by hydrogen peroxide, and the solution made up to 500 c.c.; 400 c.c. of this is then taken off by filtration, acidified with sulphuric acid, reduced with sulphurous anhydride, and evaporated to 200 or 100 c.c. This solution is then titrated against a standard solution containing 6 grams of potassium permanganate, 40 grams of potassium carbonate, and 0.5 gram of caustic potash per litre. The chromium solution is run into the boiling permanganate until the red colour gives place to the golden yellow of potassium chromate. Test analyses are given.

W. J. P.

Colorimetric Estimation of Small Quantities of Uranium in Minerals. By A. BRUTTINI (*Gazzetta*, 23, i, 251—257).—In order to separate the uranium from minerals containing it, the author treats the powdered substance with nitric acid, and eliminates the silica by evaporation to dryness and heating the residue; this is then taken up by dilute nitric acid. On adding ammonium hydrogen sulphide and ammonium carbonate to the filtered solution and heating, the uranium and arsenic and part of the antimony, tin, copper, and nickel remain dissolved, whilst all the other heavy metals are precipitated. The filtered solution is acidified with nitric acid, and, after filtration, can only contain uranium, copper, and nickel; if the last two metals are present, the uranium is precipitated with ammonia, collected, and dissolved in boiling dilute nitric acid. The uranium solution is then evaporated, the ammonium salts driven off by heat, the residue dissolved in dilute nitric acid, and the solution made up to a known volume; aliquot parts are then taken for the colorimetric determination. This is performed by means of the author's colorimeter, the depth of colour produced by mixing potassium ferrocyanide with a standard solution of uranium being compared with that obtained with the solution to be tested.

W. J. P.

Estimation of Sugar in Tomatoes. By G. C. CALDWELL (*Exper. Stat. Record*, 4, 802; from *N.Y. Cornell Stat. Bul.*, No. 49, 1882).—The fruit is dried at 100°, extracted with 90 per cent. alcohol in a continuous extracting apparatus, and the sugar determined in the extract by the gravimetric copper method. Neither the polariscope nor the Fehling test are trustworthy for direct estimation in tomatoes, on account of the possible action of organic acids and the presence of other reducing substances besides sugar.

The acidity was determined by means of standard aqueous potash, and calculated as malic acid.

N. H. M.

Detection and Estimation of Glucose by means of Phenylhydrazine. By E. LAVES (*Arch. Pharm.*, 231, 366—372).—To detect sugar in urine, 10 c.c. of it is mixed with 20 drops of phenylhydrazine and 3 grams of acetic acid, and boiled; yellow glucosazone is precipitated. To detect traces of glucose, albumin, &c., must first be pre-

cipitated with lead acetate, and the filtered solution concentrated and treated as above.

This reaction may advantageously be used to estimate glucose when the latter is present in small quantity. The solution, which should contain about 0.2 per cent. of glucose, is treated with a large excess of phenylhydrazine and acetic acid, in amounts respectively 20 and 30 times that of the glucose present, and boiled for $1\frac{1}{2}$ hours; the precipitate of osazone is collected, dried, and weighed, and a correction is applied for that left in solution. The results vary very much as the relative amounts of phenylhydrazine present alter, but the author states that the method is not inferior to that of Fehling, or to the polarimetric one, for estimating small quantities of sugar.

C. F. B.

Gravimetric Estimation of Furfuraldehyde. By W. H. KRUG (*Chem. Centr.*, 1893, i, 861; from *J. Anal. Chem.*, 7, 68—77).—Pentoses are now often estimated by converting them into furfuraldehyde by distillation with hydrochloric acid. The furfuraldehyde is then converted into the hydrazone by the addition of phenylhydrazine acetate; the precipitate should be allowed to settle for a few hours before collecting. As it adheres obstinately to the sides of the beaker, the author advises that it should be redissolved in alcohol and the solution evaporated in a tared dish. The residue is then completely dried at 60° in a current of air, and weighed.

L. DE K.

Volumetric Estimation of Acetone. By F. ROBINEAU and G. ROLLIN (*Chem. Centr.*, 1893, i, 961—962; from *Mon. Sci.* [4], 7, 272—274).—The process consists in converting the acetone into iodoform, by dissolving it in aqueous soda containing potassium iodide and adding a standard solution of sodium hypochlorite until a drop of the solution gives a blue spot on starch paper.

To standardise the hypochlorite solution, 2 grams of pure acetone is made up to 500 c.c. 100 c.c. of this solution is mixed with 10 grams of potassium iodide and 20 c.c. of aqueous soda (sp. gr. 1.24). The hypochlorite is then run in until only a faint turbidity is produced, when the starch test should be applied. Methyl or ethyl alcohol do not interfere with the process, and paraldehyde only when present in large quantity.

L. DE K.

Detection and Estimation of Thiocyanates in Ammonium Sulphate. By H. OFFERMANN (*Bied. Centr.*, 22, 507).—The ammonium sulphate obtained in coal gas purification, and used as manure, contains, according to the manner in which it is produced, more or less thiocyanate, which is injurious to vegetation. In order to detect this, the salt is extracted with absolute alcohol and the extract tested with ferric chloride solution. In estimating the amount of thiocyanate, an alcoholic solution is prepared by extracting the salt (5 grams) for an hour with methyl or ethyl alcohol. The analysis may be continued by any of the following methods: (1) colorimetrically, by comparing with an iron thiocyanate solution of known strength; (2) gravimetrically, by means of silver solution; (3) estimation of the nitrogen by Kjeldahl's method; (4)

oxidation of the residue with bromine and estimating the sulphuric acid.
N. H. M.

Estimation of Succinic acid. By A. RAU (*Zeit. anal. Chem.*, **32**, 482—486; from *Arch. f. Hygiene*, **14**, 225).—The following method was devised in the course of an investigation into the influence of varying conditions of fermentation on the formation of succinic acid. 100 c.c. of the wine is evaporated to a syrup, extracted repeatedly with boiling alcohol, and the cooled alcoholic solutions filtered, mixed, and distilled. The residue is dissolved in a little hot water, and the cooled solution filtered, if turbid; it is then treated with barium nitrate, 3—4 vols. of 90 per cent. alcohol are added, and the mixture is well stirred. The precipitate, containing tartaric, malic, and succinic acids, is collected, washed well with 70 per cent. alcohol, warmed with sodium carbonate solution, and filtered; the filtrate is neutralised with nitric acid, evaporated to a small bulk, and, after neutralisation with ammonia, is precipitated with a magnesia mixture, made with magnesium nitrate, ammonium nitrate, and ammonia. The precipitate, which contains the tartaric acid, is filtered off after three or four hours' repose; the filtrate is heated with potash until all the ammonia is expelled, then filtered from magnesia, neutralised exactly with nitric acid, diluted to 100—150 c.c., and precipitated with silver nitrate (1 : 20). Silver nitrate precipitates succinic acid completely, but produces precipitates in malic acid solutions only when they are stronger than 1 : 800. The precipitate is collected on a tared filter, washed well, dried, and weighed. As a control, it may be ignited and the silver weighed. Should the solution, to which silver nitrate is to be added, contain chlorides, which may happen if too much alcohol has been added after the barium nitrate, or too long an interval has been allowed before filtration, a portion of it must be evaporated, incinerated, the chlorine determined, and a corresponding quantity of silver chloride subtracted from the weight of the silver succinate. Proof estimations gave 102, 98·7, and 103 per cent. when working with 0·1 gram in 100 c.c.

The fermentation experiments show that a low temperature does not diminish the production of succinic acid; that the absence or presence of air is without influence; that the addition of nutrient substances does not favour its formation; but that an increased production is induced by a vigorous action of the yeast cells.

M. J. S.

Examination of Tartaric and Citric acids for Lead. By M. BUCKET (*Zeit. anal. Chem.*, **32**, 465; from *Répert. Pharm.*, **48**, 246).—200 grams of the substance is dissolved in 600 c.c. of water, and made feebly alkaline with ammonia. Any insoluble matter is collected, washed, dissolved in nitric acid, and the lead precipitated by sulphuric acid and alcohol. The lead thus found was originally present in the metallic state. The ammoniacal solution is now acidified with hydrochloric acid, and precipitated with hydrogen sulphide solution. The lead sulphide is converted into the sulphate in the same way as above; its amount gives the lead originally present as lead compounds.

M. J. S.

Calcium Tartrate from Distillery Residues ; its Estimation and Purification. By C. ORDONNEAU (*Bull. Soc. Chim.* [3], 9, 66—70).—The process adopted in order to obtain calcium tartrate from the vinasse is to saturate the latter with lime; if, however, it contains other acids, such as malic, in addition to tartaric, then lime is added in amount insufficient for complete neutralisation; in this case, the calcium tartrate precipitated is fairly pure, whereas, had the solution been neutral, instead of still acid, much malate would also have been precipitated.

To estimate tartaric acid in a mixture of calcium tartrate and malate, 20 grams of the powdered substance is dissolved in 20 c.c. of hydrochloric acid and 80 c.c. of water, and the whole made up to 202 grams if the original substance contains more than 75 per cent. of tartrate, to 203 grams if it contains less. 50 c.c. of the solution is taken, 2 c.c. of a 25 per cent. solution of citric acid (to dissolve aluminium phosphate) and 10 c.c. of 25 per cent. calcium acetate added, and the mixture shaken violently. After a precipitate has formed, 5 c.c. more acetate is added, the mixture shaken, allowed to settle for half an hour, collected, and washed. The precipitate is dried on the filter on a copper plate over a water-bath, transferred as completely as possible to a nickel capsule, and heated on the water-bath with constant stirring until the moment when the clots of moist tartrate break up into a fine powder; the salt then contains $4\text{H}_2\text{O}$. Its weight multiplied by 20 gives the percentage of calcium tartrate in the substance examined, after adding 2 per cent. to allow for what is left on the filter paper and dissolved in the calcium chloride. Or 50 c.c. of the solution is taken as before, heated to boiling in a porcelain capsule, neutralised with clear lime-water, using phenolphthaleïn as indicator, 2 c.c. of 25 per cent. citric acid solution added, and the precipitate collected, washed, dried, and weighed as before, adding this time 4 per cent. to the result, as calcium tartrate is more soluble in a hot solution of calcium chloride. C. F. B.

Estimation of Uric acid. Behaviour of Uric acid in Solution. By I. KREIDL (*Monatsh.*, 14, 109—115).—To the solution of uric acid, a moderate excess of (normal) potash solution is added, and then a considerable excess of N/30 iodine solution; after standing for three-quarters of an hour, the solution is acidified with hydrochloric acid. The excess of iodine then separates, and is titrated with N/30 thiosulphate, starch being used as an indicator; 3.5 atoms of iodine correspond with 1 mol. of uric acid under these circumstances, and 2.3 if the hydrochloric acid is added immediately after the iodine solution. A solution of uric acid, and still more one of potassium urate, when allowed to remain in contact with air, gradually loses its power of reducing iodine solution, but this is due to the presence of microbes, for a sterilised aqueous solution of uric acid does not undergo this change in a sterilised atmosphere; potassium urate does, however, if the solution is boiled, or if a slight excess of potash is present. C. F. B.

Estimation of Solids and Fat in Milk. By J. B. KINNEAR (*Chem. News*, 68, 1—2).—The following process may be used either for cream or for rich or skimmed milk. About 1 gram of milk is poured on to a thin, flat tared glass plate, about $2\frac{1}{2}$ inches in diameter, and after weighing is dried in a hot air chamber, being loosened from the glass by a steel scraper before it is quite dry. The dry solids are weighed and transferred to a $\frac{1}{2}$ -oz. tared stoppered bottle, 3 to 4 c.c. of ether is then added, the stopper tied down, and the bottle immersed in warm water for a few minutes, shaken for one minute, then cooled and weighed. As much of the clear solution as possible is now poured into a tared watch glass, the stopper immediately replaced, and the bottle again weighed. The fat on the watch glass is also weighed, and from the data obtained, the fat remaining in the bottle, the total fat in the ether and in the milk are calculated. The error arising from the evaporation of the ether during the pouring out into the watch glass is in the author's opinion a negligible quantity for practical purposes, and almost disappears if light petroleum is used as the solvent. D. A. L.

The Elaïdin Reaction. By A. LIDOFF (*J. Russ. Chem. Soc.*, 24, 515—524).—Oils which do not dry become solid when treated with nitrous acid, on account of the conversion of the oleïn they contain into elaïdin. Drying oils, on the other hand, remain liquid under similar treatment, although at the same time their chemical and physical properties are considerably modified. Their sp. gr. increases as well as their viscosity and saponification ratio. The iodine coefficient and Hehner's ratio diminish. All oils after treatment with nitrous acid contain nitrogen, varying in amount from 1 to 2·5 per cent. These substances may be reduced by various agents, yielding new substances which probably contain the amido-group. The free unsaturated acids yield no such compounds. J. W.

Estimation of Caffeïne. By A. GRANDVAL and H. LAJOUX (*J. Pharm.* [5], 27, 545—549).—The finely powdered material (5 grams) is stirred with a well shaken mixture of ether (5 grams) and officinal (French) solution of ammonia (1 gram) in a porcelain capsule; the powder is then completely extracted with chloroform (50 c.c.) in a reflux extraction apparatus, the chloroform is driven off from the extract, and the residue, after being moistened with 10 per cent. sulphuric acid (1 c.c.), is extracted several times, to complete exhaustion, with small quantities of hot water, and the aqueous solution is filtered, the funnel being covered with a watch-glass. In the case of roasted coffee, the aqueous solution is made alkaline with soda, and completely extracted with chloroform, the chloroform extract is evaporated, and the residue of caffeïne is weighed. In other cases, the solution is treated with excess of ammonia, evaporated, the residue completely extracted with chloroform, the chloroform extract filtered and evaporated, and the residue of caffeïne weighed. The process is accurate, and takes only three hours to perform. Black tea contains 2·9, raw coffee 0·988, roasted coffee 0·9, and kola nut 2·3 per cent. of caffeïne. C. F. B.

Estimation of Emetine in Ipecacuanha Root. By C. KELLER (*J. Pharm.* [5], 27, 465—467; from *Pharm. Post*, 25, 913; compare this vol., ii, 398).—The methods of Flückiger, Kremel, and Lloyd were tried and found defective; the following is recommended:—Powdered ipecacuanha (15 grams) is placed in a flask with alcohol of 90° (148 c.c.) and some hydrochloric acid (2 c.c.; sp. gr. = 1.12), the flask is corked, and the mixture digested for four days at 40°, being frequently shaken. When cold, 100 c.c. of the clear liquid is withdrawn, mixed with 20 c.c. of a solution of neutral lead acetate (1 gram) in 50 per cent. alcohol (10 grams) and 1.5 grams of slaked lime, and evaporated on the water bath to a thin paste; it is then mixed with 5 grams of powdered glass, and evaporated to dryness, with frequent stirring. The dry mass, after being powdered, is extracted with chloroform, the chloroform is driven off from the extract, and the residue weighed. It is then treated with 2 c.c. of normal hydrochloric acid, and washed with water; the residual resin is weighed, and its weight subtracted from that of the first residue; the difference is the weight of the emetine, which was dissolved out by the hydrochloric acid. Various specimens of ipecacuanha examined contained from 1.81 to 2.37 per cent. of emetine.

C. F. B.

Analysis of Ethereal Oils. By R. BENEDIKT and H. STRACHE (*Monatsh.*, 14, 270—277).—As an aid in the identification of ethereal oils, the authors have determined the “carbonyl number” (“Carbonylzahl”) for many of these, that is, the amount of carbonyl oxygen in 1000 parts of the oil. The value of this coefficient varies from 0.9 in the case of oil of cedar wood to 145.3 in the case of oil of bitter almonds; it has been determined for a number of different oils and their commercial varieties, but the table of results is too long to reproduce. The method adopted is to boil a weighed quantity of the oil with phenylhydrazine hydrochloride (the relative amounts varying as the oil contains more or less carbonyl oxygen) and sodium acetate in amount equal to $1\frac{1}{2}$ times that of the hydrochloride for a quarter of an hour in alcoholic solution. The whole is then made up to 100 c.c., the hydrazone and unattacked oil filtered off through a dry folded filter, and the excess of phenylhydrazine determined by oxidising 50 c.c. of the filtrate with hot Fehling's solution, and measuring the nitrogen evolved (*Abstr.*, 1892, 1322). An improved method of measuring the nitrogen is described.

C. F. B.

Hüfner's Method of estimating Urea. By W. CAMERER (*Zeit. Biol.*, 29, 239—246).—It is urged that this method of estimating urea is of sufficient accuracy for all purposes. There are certain points of detail to be attended to which are pointed out. Among the facts noted may be mentioned the following. The alkaline solution need not be absolutely fresh for every estimation; keeping for 24 hours makes only a very small difference in the result. The yield of nitrogen from urine is slightly greater when sugar is added, but not sufficient to account for the increase of urea found in diabetes.

W. D. H.

General and Physical Chemistry.

Absorption of Light by Liquid Bromine. By C. CAMICHEL (*Compt. rend.*, 117, 307—309).—Liquid bromine, even in layers not greatly exceeding in thickness a wave-length of the line D, has a very energetic absorbing action. Measurements made with a Gouy spectrophotometer on very thin layers of bromine enclosed between glass plates such as serve for the production of Newton's rings, show that when the abscissæ are the thicknesses of the layer of bromine, and the ordinates are the values of $\log I_2/I_1$, the results are represented by right lines. The absorption of thin layers of bromine, therefore, follows the exponential law. The coefficients of absorption are, for λ 589 (Na), 0.517×10^3 ; for λ 569, 0.981×10^3 ; and for λ 535 (Ti), 2.49×10^3 .
C. H. B.

Product of Asymmetry. By P. A. GUYE (*Compt. rend.*, 116, 1378—1379).—The product of asymmetry is defined as the product of the six perpendiculars drawn from the centre of gravity of a tetrahedron to the six planes of symmetry. If the masses of the four groups united to a carbon atom are either placed at the four angles of the regular tetrahedron, or at variable distances from these, or are laterally displaced, the above product will be represented in each case by a formula of a more or less complex nature. The author deduces general expressions for the product in the cases named, but, as each of these contains a number of unknowns, it is impossible to put them to a strict experimental verification. Some general applications will, however, be given later.
H. C.

Rotatory Power of a Substance belonging to an Homologous Series. By P. A. GUYE (*Compt. rend.*, 116, 1451—1454).—The author considers, with the aid of the formulæ for the product of asymmetry deduced in former papers (this vol., ii, 204, and preceding abstract), the effect on the rotatory power of a substance *Cabcd* that will be produced by a gradual and regular increase in the mass of *a*. If the asymmetry of the molecule is not very pronounced, a gradual increase in *a* may have the effect of increasing the rotatory power until a maximum is reached, from which a decrease will take place. If the asymmetry is of a very pronounced character, the change in the rotatory power may be of various kinds, but it is not possible to give general rules for these cases.
H. C.

Rotatory Power of Ethereal Salts of Valeric and Glyceric acids. By P. A. GUYE and L. CHAVANNE (*Compt. rend.*, 116, 1454—1457).—In order to submit certain deductions, made by one of the authors with regard to the rotatory powers of substances belonging to an homologous series (preceding abstract), to the test of experiment, the rotatory powers of certain ethereal salts of valeric acid have been measured. Among the alkyl salts, the methyl compound

is found to have the greatest rotation, greater than that of the acid itself, a maximum in rotatory power therefore existing in this place, as predicted by theory. The rotatory powers of ethereal salts of glyceric acid, measured by Frankland and MacGregor (*Trans.*, 1893, 511), also rise to a maximum in the case of the alkyl salts, this occurring, in this instance, with the propyl compound. H. C.

Influence of Organic Solvents on Rotatory Power. By FREUNDLER (*Bull. Soc. Chim.*, [3], 9, 409—413).—The rotatory power of ethereal salts of the type $\text{COOR} \cdot \text{CHO}(\text{R}'\text{CO}) \cdot \text{CHO}(\text{R}'\text{CO}) \cdot \text{COOR}$ is compared with the corresponding quantity deduced from observations on their solutions in dry acetone, absolute alcohol, 94 per cent. alcohol, benzene, chloroform, and carbon tetrachloride respectively. Measurements were made at temperatures kept nearly constant, the extreme limits being 20° and 28° .

Dry acetone, absolute alcohol, and 94 per cent. alcohol have very little effect on the rotatory power at concentrations of about 1 gram in 20 c.c. of the solvent.

Benzene, chloroform, and carbon tetrachloride lower the algebraic value of the rotatory power to a considerable extent, differing with the solvent used. Probably molecular compounds are formed between these solvents and the ethereal salts, a view upheld by the fact that increase of temperature increases algebraically the rotatory power, bringing this quantity nearer to its normal value as the conditions become more favourable to the dissociation of molecular combinations. The temperature effect is marked with chloroform solutions.

In acetone solutions, the rotatory power decreases slowly as the concentration increases; in chloroform solutions, the reverse is the case beyond a certain concentration. If the formation of molecular combinations be admitted, this fact is readily explained by the increasing difficulty of forming the compound, as less of the solvent remains free. W. T.

A One-Volt Standard Cell. By H. S. CARHART (*Amer. J. Sci.*, [3], 46, 60—66).—The author employs a one-volt standard cell, of the same form as the Clark standard. The tube contains pure mercury in contact with a platinum wire; on this is placed mercurous chloride paste, covered with zinc chloride solution. A cork diaphragm, with asbestos packing under it, is employed to keep the paste in position, and above it is placed more zinc chloride solution containing an amalgamated zinc rod; the whole is then hermetically sealed. The sp. gr. of the zinc chloride solution necessary to give an E.M.F. of 1 volt at 13.7° is 1.391 at 15° . The internal resistance of the cell is about 1500 ohms, and it seems to suffer no permanent change by heating at 50° . It is noteworthy that this cell has a positive and very small temperature coefficient; from 10° to 40° the temperature curve is approximately a straight line, and the E.M.F. is obtained from the equation $E_t = 1 + 0.000094(t - 15)$. Above 40° , the curve rises and involves the third power of $t - 15$. The E.M.F. is observed to lag somewhat as the temperature falls; the hysteresis is, however, very slight, being equivalent to about 3° difference of temperature.

The sign of the temperature coefficient of standard cells depends on the relative magnitudes and signs of the thermo-E.M.F.'s at the two sides of the couple. These may be experimentally determined by means of an H-tube containing the solution and electrodes of the metal concerned; one limb of the tube is kept in melting ice, and the other in a bath at the required temperature. The E.M.F. set up is determined electrostatically, and is balanced against a standard E.M.F. Employing this method, the author has measured the thermo-E.M.F. of the voltaic series $\text{Cu} \mid \text{CuSO}_4 \mid \text{Cu}$ between 0° and 50° as $+0.00073$ volt, and has hence calculated the values for several other series, and compared them with the experimental values. The data given by Bouty, and by Chroustchoff and Sitnikoff (*Compt. rend.*, 108, 937), would show the temperature coefficient of the author's cell to be small but negative. Bouty's thermo-E.M.F. for the series $\text{Zn} \mid \text{ZnCl}_2 \mid \text{Zn}$ is, however, too large; the author finds it to be 0.000584 , a number from which the temperature coefficient of the new cell is calculated as practically identical with the value obtained experimentally.

W. J. P.

Electrical Conductivity of Flames and Gases. By A. DE HEMPTINNE (*Zeit. physikal. Chem.*, 12, 244—274).—Two platinum electrodes were so connected, one with a galvanic element and the other with a capillary electrometer, that the presence of a conducting substance between them was indicated by the mercury in the electrometer assuming a negative charge and moving upwards in the capillary. No effect was noticed when the electrodes were immersed in nitric oxide and oxygen gases in the act of combining, even when the electromotive force employed was 100 volts. The same negative result was obtained when the reacting pairs of gases were hydrogen bromide and chlorine, and hydrogen chloride and ammonia.

The influence of temperature was noted by placing the electrodes at the same relative part of a bunsen flame, the combustible gas containing variable quantities of an indifferent gas. The hydrogen flame and the carbonic oxide flame conduct well, the conductivity increasing with rise of temperature.

Observations were also made on the conductivity of explosive mixtures at the moment of explosion. There is decided conductivity in the case of oxygen-hydrogen and chlorine-hydrogen explosions, and a much slighter amount in the case of oxygen-carbonic oxide.

Although hydrogen chloride and ammonia show no conductivity by themselves at moderate temperatures, dissociating ammonium chloride conducts fairly well. Ammonium bromide behaves similarly, but vapour of amylene bromide (although it is dissociated) does not conduct. Nitric oxide is a non-conductor.

J. W.

Experiments with the Manocryometer. By L. E. O. DE VISSER (*Rec. Trav. Chim.*, 12, 101—140).—The "manocryometer" employed by the author is a stout glass vessel, resembling Ostwald's modification of the Sprengel density tube. The short capillary is sealed off, and the long capillary has two small bulbs on the ascending portion, the horizontal part being very long and sealed at the end. The purpose of the apparatus is to determine the melting point of a sub-

stance under pressure. The principal bulb (46 c.c.) is filled with the experimental substance, the lower part of the capillary and the lower bulb with mercury, the upper bulb (1.3 c.c.) and the rest of the capillary (0.13 c.c.) being filled with air, which acts as a manometer. The substance is heated to a temperature (constant within 0.001°) a little above its melting point for half an hour, and the pressure is then read off. This gives the value $\frac{dT}{dp}$ in James Thomson's formula

$$\frac{dT}{dp} = 10333 \cdot \frac{T}{E} \cdot \frac{\sigma - \tau}{r}. \quad \text{The author determined } \frac{dT}{dp}, T, \sigma, \sigma - \tau,$$

and r for acetic acid, as well as the value $\frac{\sigma - \tau}{r}$, directly by the use of an acetic acid calorimeter analogous to Bunsen's ice-calorimeter. His results are as follows.

Melting point of acetic acid (T) at 760 mm. = 16.6713° (mercury thermometer), or 16.5965° (hydrogen thermometer).

Sp. gr. of liquid at melting point = 1.05315 compared with water at 4° , whence sp. vol. (σ) = 0.94953.

Change of volume on fusion of 1 kilo. in cubic metres ($\sigma - \tau$) = 0.00015955, whence sp. vol. of solid (τ) at melting point = 0.78998, or sp. gr. of solid at the melting point = 1.26585.

Heat of fusion (r) at melting point = 46.416 Cal.

$$\frac{\sigma - \tau}{r} \text{ calculated} = 0.0000034374.$$

$$\frac{\sigma - \tau}{r} \text{ found directly} = 0.0000034425.$$

$$\frac{dT}{dp} \text{ calculated from Thomson's formula} = 0.02421^\circ.$$

$$\frac{dT}{dp} \text{ observed with manocryometer} = 0.02435^\circ.$$

J. W.

The Speed of Vaporisation of Compounds in Different Atmospheres. By R. D. PHOOKAN (*Zeit. anorg. Chem.*, 5, 69—74).—The author has already shown that the time of vaporisation of a compound in atmospheres of vapours of different densities is constant (*Zeit. anorg. Chem.*, 2). In this paper he points out some sources of error in his earlier experiments, and figures an improved apparatus. From the table comprising his results, it appears that the quantity of normal propyl alcohol used in the experiments varied from 0.0264 to 0.0268 gram; that the volume of vapour measured varied from 13.7 to 15.0 c.c., and that the time of vaporisation in vapour of methyl alcohol, ether, chloroform, perchloromethane, and in hydrogen varied from 12 to 14 seconds, whilst the same value in air was 23 seconds, and in carbonic anhydride 26—27 seconds.

A. G. B.

Diffusibility of certain Gases through a Caoutchouc Membrane. By A. REYCHLER (*Bull. Soc. Chim.*, [3], 9, 404—409).—Sulphurous anhydride combines with caoutchouc just as it combines

with camphor. In an atmosphere of sulphurous anhydride, caoutchouc absorbs the gas with consequent reduction of pressure; under reduced pressure, or in the air, the absorbed gas is given off, increasing the partial pressure due to the sulphurous anhydride. Hence the explanation of the apparently abnormal diffusion of sulphurous anhydride and carbonic anhydride through membranes of caoutchouc. When a tube, closed at one end with a thin caoutchouc membrane, is inverted over mercury and filled with sulphurous anhydride, or a mixture of sulphurous anhydride and carbonic anhydride, the mercury rises in the tube, as observed by Pictet, not because of any abnormal diffusibility of these gases through caoutchouc, but because a compound is formed with the caoutchouc reducing the pressure within the tube and almost simultaneously the gas absorbed is given off from the upper surface of the membrane by the decomposition of this compound in the free air. The true diffusion of atmospheric gases through the septum in the opposite direction is so comparatively slow that the pressure in the tube is brought almost to zero.

With thicker membranes, the penetration of the gas to the outer surface is greatly hindered, and hence the rate of apparent diffusion is lowered. Carbonic anhydride traverses caoutchouc at a much slower rate than sulphurous anhydride. W. T.

Diffusion in Aqueous Solutions of Mixed Salts. By L. LIEBERMANN and S. BUGARSKY (*Zeit. physikal. Chem.*, **12**, 188—195).—Suppose a solution, A, containing 1 gram-molecule of sodium chloride and 1 gram-molecule of potassium nitrate per litre is brought into diffusion-contact with a solution, B, containing 1 gram-molecule per litre of sodium chloride; then, if double decomposition takes place in the first solution with consequent formation of some potassium chloride and sodium nitrate, sodium chloride will diffuse from B to A, and potassium chloride from A to B. Since the rates of diffusion of these salts are different, the amount of chlorine in different parts of the solution should vary. If, however, Arrhenius' theory is correct, and all the salts are dissociated into ions, no double decomposition can take place and the amount of chlorine in different parts of the solution will remain the same, although the relative amounts of potassium and sodium go on varying.

The authors have conducted experiments of this nature, and find that there is no appreciable variation in the amount of chlorine in the different parts of the solution. J. W.

Dissociation Ratio of Salts. By A. A. NOYES (*Zeit. physikal. Chem.*, **12**, 162—166; compare *Abstr.*, 1892, 1143).—While admitting the applicability of the method proposed by Arrhenius for deciding between the respective values of the electrolytic conductivity and the influence on solubility for determining the dissociation ratio of salts in aqueous solution, the author denies the validity of Arrhenius' conclusions (this vol., ii, 364). J. W.

Freezing Point of Solutions of Sodium Chloride. By S. U. PICKERING (*Ber.*, **26**, 1977—1979).—A rejoinder to Jones (this vol., ii, 447).

Nature of certain Solutions and a new means of investigating them. By M. C. LEA (*Amer. J. Sci.*, [3], **45**, 478—487).—"Herapathite" (the double sulphate and hydriodide of quinine tetriodide) is converted by digestion with barium carbonate in alcoholic suspension into a substance which contains no sulphuric acid and is soluble in alcohol, and this substance is reconverted by the smallest trace of free sulphuric acid into an equivalent amount of herapathite.

In applying the test, the finely-powdered crystals are covered with cold 70 per cent. alcohol, and repeatedly digested with excess of barium carbonate until crystals of herapathite are no longer deposited when a portion of the solution, made acid with a little oxalic acid, is allowed to evaporate spontaneously. The liquid to be tested is mixed with alcohol and some of the solution, when, if more than a trace of free sulphuric acid be present, a black precipitate of herapathite at once appears. With quantities even as minute as 0.000015 gram of acid, a distinct film of microscopic crystals is formed on evaporating the mixture. The presence of neutral sulphates does not affect the reaction.

According to this test, the solutions of the sulphates of the alkalis (normal), of magnesium, zinc, cadmium, copper, nickel, cobalt, manganese, and thallium, and of the alkaloids morphine, quinine, strychnine, and brucine, do not contain free sulphuric acid. The acid reaction shown by some of these substances towards litmus is due to dissociation of the unstable metallic salt of the litmus acid formed by double decomposition, an explanation supported by the fact that alkaloids, brucine for instance, precipitate the hydroxides of zinc, cadmium, copper, manganese, nickel, and cobalt from solutions of these sulphates; solutions of ferrous sulphate and its ammonium and magnesium double salts show an acid reaction, probably due to ferric sulphate. Solutions of chromium, aluminium, glucinum, and ferric sulphates all contain a considerable amount of free sulphuric acid. Solutions of potash alum, ammonium iron alum, and manganese alum contain free acid, but a solution of potassium chrome alum does not do so. A solution of sodium hydrogen sulphate contains free acid.

JN. W.

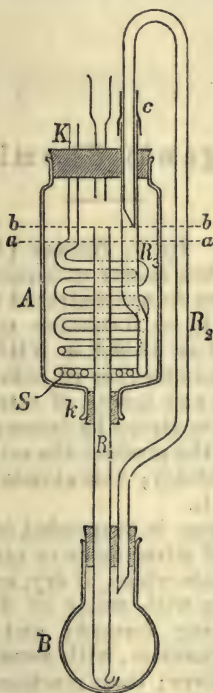
Conditions of Chemical Equilibrium. Part II. By S. BUGARSZKY (*Zeit. physikal. Chem.*, **12**, 223—229).—The author, in a former paper (this vol., ii, 450), found that the action of potassium bromide on mercuric oxide did not take place according to the law of mass action when conceived as $2\text{KBr} + \text{HgO} + \text{H}_2\text{O} = 2\text{KOH} + \text{HgBr}_2$. He now finds, however, that the reaction is really $4\text{KBr} + \text{HgO} + \text{H}_2\text{O} = 2\text{KOH} + \text{K}_2\text{HgBr}_4$, and that the law of mass action is obeyed.

J. W.

Lecture Experiment with the Manocryometer. By L. E. O. DE VISSER (*Rec. Trav. Chim.*, **12**, 154—156).—A tube of 2 mm. internal diameter, with walls 6 mm. thick, is sealed off at one end and drawn out to a capillary at the other, the whole being about 15 cm. long. This tube is immersed in pure acetic acid and filled by alternately exhausting and admitting air over the acid. The tube is now inverted and the capillary end is plunged into the acetic acid, the wide portion

being cooled by wrapping it in cotton wool on which ether is dropped. The contents solidify with considerable diminution of volume, fresh acid being sucked up. The greater portion of the acid having solidified, the capillary is withdrawn from the acid, and the cooling is continued until air has entered the capillary, which is then sealed off. The tube is now ready for use, and is suspended in a beaker of water, the temperature of which is gradually increased. Acetic acid melts at 16.6° at the ordinary pressure, but when thus confined in a closed space it greatly increases the pressure as it melts, so that the freezing point of the remaining solid is raised. The author has succeeded in raising the freezing point as high as 40° , corresponding with a pressure of about 100 atmospheres. The tubes, when they break, do not explode, but merely crack lengthwise. J. W.

New Extraction Apparatus. By C. T. L. HAGEMANN (*Ber.*, 26, 1975—1977).—The apparatus figured below has been devised by the author for extracting liquids (aqueous solutions) with solvents. The vessel *A* is charged as far as the dotted line *aa* with the solution to be extracted. The extracting agent (usually ether) is placed in the



flask *B*, which is heated on a water bath; its vapour passes upwards through the tube *R*₂, into a glass spiral *S*, which is pierced above and sideways with small holes by which the vapour escapes and passes

through the solution to be extracted. It condenses and forms a layer on the upper surface of the solution; when the layer is above *bb*, it flows back into the flask *B* through the tube *R*₁.

In order that the solution in *A* may not become heated to the boiling point of the ether, which causes violent bubbling of the entire liquid, so that a portion of the aqueous solution is sometimes carried over into the flask *B*, it is necessary to employ a cooling worm, *K*; a reflux for the ether is, however, unnecessary. The ether should be kept in gentle ebullition, and to ensure this, pieces of unglazed porcelain are introduced into the flask *B*.

When using the apparatus with extracting agents heavier than water (chloroform, for example), the spiral *S* is placed in the upper portion of the solution, and above the latter is arranged a condenser. A wider tube, open at both ends, is then placed over the tube *R*₁, and before commencing the experiment, a small quantity of the extracting agent is poured on to the bottom of the vessel *A*. The vapour of the extracting agent condenses in drops which fall through the solution and collect at the bottom of *A*. The extracting agent rises in the space between the two tubes just described until it overflows through *R*₁ into the flask *B*.

A. R. L.

Inorganic Chemistry.

Iodide of Nitrogen. By J. SZUHAY (*Ber.*, 26, 1933—1945).—The compound formed when excess of aqueous ammonia is added to a strong solution of iodine in concentrated aqueous potassium iodide has the composition NHI_2 , its formation taking place according to the equation $3\text{NH}_3 + 4\text{I} = 2\text{NH}_4\text{I} + \text{NHI}_2$. This was ascertained by finding the ratio of the amounts of iodine, contained respectively in the ammonium iodide and iodide of nitrogen, formed to be 1 : 1. The latter substance was analysed by decomposing it with sulphurous acid, and determining in the product the ratio of nitrogen (present as ammonia) to iodine (as iodide); this atomic ratio is 1 : 2, corresponding with the formula NHI_2 .

When iodide of nitrogen is suspended in water, and treated with an ammoniacal solution of silver oxide or nitrate, a compound NAgI_2 is formed, a black substance which, if dry, explodes when heated. It is decomposed by boiling with water or dilute acids, silver iodide, iodine, and nitrogen being formed; and is reduced by sodium amalgam or metallic aluminium, with formation of ammonia, hydriodic acid, and metallic silver; these reactions were used to determine its composition. By treating this silver compound with a soluble cyanide, the metal of the latter can be made to replace the silver; the resulting substances are not well characterised, but can be reconverted into the silver compound.

C. F. B.

Existence of Nitrous acid in Aqueous Solution. By L. MARCHLEWSKI (*Zeit. anorg. Chem.*, 5, 88—91).—The author argues that if an aqueous solution of N_2O_3 is a conductor of electricity, it can only be so by virtue of the presence of nitrous acid, there being H and NO_2 ions in the solution. Liquid nitrous anhydride, made from arsenious acid and nitric acid (sp. gr. 1.35), is introduced into a pipette, provided with a stopcock on its stem; the pipette is ground into the neck of a separating funnel, which has two electrodes sealed in its side in such a position that the point of the pipette is just between them. The funnel is full of water, and the liquid is forced into it by a stream of cold water, introduced through the stem of the pipette. It is noted that the solution allows a current from four Daniell cells to pass, and analysis of the liquid withdrawn through the stopcock of the separating funnel indicates that only nitrous acid can be present. The author is satisfied that nitrous acid can exist in aqueous solution, and that there is thus no ground for doubting its existence in dilute nitric acid (compare Armstrong, *Proc.*, 1893, 151).

A. G. B.

Decomposition of Gaseous Hydrogen Phosphide. By D. M. KOOLJ (*Zeit. physikal. Chem.*, 12, 155—161).—The author has made observations on the rate of decomposition of gaseous hydrogen phosphide at different temperatures, and finds the temperature variation of the constant of velocity k to be expressible by means of an equation of the form $\log k = A/T + B \log T + C$, as theory predicts.

Temp.	k .	k (calc.).
512°	0.0081	(0.0081)
446	0.0025	(0.0025)
367	0.00067	0.00061
310	0.00021	(0.00021)

J. W.

Hexametaphosphates. By H. LÜDERT (*Zeit. anorg. Chem.*, 5, 15—41).—The following salts were prepared by double decomposition between the salts of the metals and the sodium hexametaphosphate obtained by heating sodium ammonium hydrogen phosphate:—(a) As flocculent precipitates, $\text{Ag}_6\text{P}_6\text{O}_{18}$; $\text{Pb}_3\text{P}_6\text{O}_{18}$; $\text{Ba}_3\text{P}_6\text{O}_{18}$; $\text{Sr}_3\text{P}_6\text{O}_{18}$; $\text{Hg}_6\text{P}_6\text{O}_{18}$. (b) As gelatinous substances, $\text{Cu}_3\text{P}_6\text{O}_{18}$; $\text{Ca}_3\text{P}_6\text{O}_{18}$; $\text{Mn}_3\text{P}_6\text{O}_{18}$; $\text{Fe}_3\text{P}_6\text{O}_{18}$; $\text{Ni}_3\text{P}_6\text{O}_{18}$; $\text{Hg}_3\text{P}_6\text{O}_{18}$.

A. G. B.

Sulphides of Phosphorus. By A. HELFF (*Zeit. physikal. Chem.*, 12, 196—222).—Observations of the boiling point of carbon bisulphide containing various proportions of sulphur and phosphorus in solution show that no combination between these two substances takes place at the temperature of the boiling solvent. The melting point of mixtures of phosphorus and sulphur is a linear function of the concentration, which shows that the two liquid sulphides of phosphorus, P_4S and P_4S_2 , are merely solutions of sulphur in phosphorus. The molecular weight of sulphur dissolved in phosphorus, as determined from the depression of the freezing point, agrees very nearly with the formula S_8 .

By heating 4 atoms of red phosphorus with 3 atoms of sulphur, the author obtained only one substance, P_4S_3 ; but by heating the elements together in the proportion of 2 atoms of red phosphorus to 3 atoms of sulphur, two sulphides of phosphorus were obtained, P_4S_7 with a small quantity of P_4S_3 . The substance P_3S_6 was formed when the elements were heated together in the theoretical proportions. When 5 atoms of sulphur were heated with somewhat more than 2 atoms of red phosphorus, only the compound P_2S_5 was obtained. The author thus concludes that the following substances are the chemical compounds of phosphorus and sulphur: P_4S_3 , P_4S_7 , P_3S_6 , and P_2S_5 .

J. W.

Sublimation of Arsenic. By J. W. RETGERS (*Zeit. anorg. Chem.*, 4, 403—409).—On heating arsenic in a glass tube closed at the lower end, a sublimate is obtained consisting of several parts. Arsenious anhydride condenses on the part of the tube furthest from the flame; immediately below this is deposited a velvety-black, perfectly opaque ring of arsenic, which is usually described as consisting of amorphous arsenic. This ring is followed by a brown, transparent deposit, separating it from a silver-white sublimate of metallic lustre; the latter consists of ordinary, hexagonal arsenic, the crystals being fairly large. Cubic crystals of arsenious anhydride are observed in all parts of the sublimate; they exhibit the octahedron form, and very rarely the triakisoctahedron. The so-called amorphous arsenic is not really amorphous; the thinner parts of the deposit under a very high power are seen to consist of a number of isolated points which reflect light. It is therefore crystalline, and the crystals probably belong to the cubic system; many unsuccessful attempts were made to obtain larger crystals for microscopic examination. The brown deposit separating this from the sublimate of hexagonal arsenic seems not to have been previously noticed; it is transparent and quite amorphous, is dissolved by boiling water, and consists of an oxide of arsenic, probably the suboxide of Berzelius. A deposit of similar appearance to this is obtained by condensing the flame of hydrogen which has been passed over heated arsenic on cold porcelain; this deposit, however, probably consists of Janowsky's solid arsenic hydride, AsH_2 or As_2H_4 . It dissolves in methylenic iodide, xylene, and concentrated potash, and is immediately oxidised to the metallic state by gold chloride, but not by stannic or mercuric chloride. The hydride and the suboxide are easily distinguished by their behaviour towards ammoniacal silver solutions; the former immediately reduces the solution with deposition of metallic silver, whilst the suboxide only becomes reduced after some time. No liquid could be found which acts simply as a solvent of metallic arsenic. Even in the finest state of subdivision arsenic is quite opaque; all observations of yellow or brown transparent arsenic are merely due to confusion with oxide or hydride.

W. J. P.

Boron Carbide. By O. MÜHLHAUSER (*Zeit. anorg. Chem.*, 5, 92—93).—This compound is produced by heating a mixture of boric anhydride and carbon in the electric furnace. The graphite-like mass is heated in a platinum crucible for $5\frac{1}{2}$ hours, powdered, boiled with hydrochloric acid, filtered, washed, again boiled with hydro-

chloric acid, and finally treated with hydrofluoric and sulphuric acids. Analysis shows it to have the formula BC or B_2C_2 . It is a black powder, having much the same properties as graphite. At a high temperature it becomes soft, and at a very high temperature it melts. It burns with difficulty in oxygen. It is insoluble in nearly all the usual solvents, but is decomposed by fusion with alkalis.

A. G. B.

Behaviour of Charcoal with Halogens, Nitrogen, Sulphur, and Oxygen. By W. G. MIXTER (*Amer. J. Sci.*, **45**, 363—379).—Hydraulically-compressed sugar charcoal containing 0.13 per cent. of hydrogen and 0.04 per cent. of ash absorbs about 4 per cent. of chlorine at a red heat, and does not give it up in a vacuum at that temperature. The chlorine cannot be displaced by nitrogen, but can be removed by hydrogen. At the ordinary temperature, little or no chlorine is absorbed. Bromine and iodine are less easily absorbed, and more easily lost. Lamp-black absorbs more chlorine, and both charcoal and lamp-black lose it at the temperature at which porcelain softens. Gas carbon, graphite, and diamond are not affected by chlorine. Charcoal, after ignition in hydrogen chloride, contains 0.26 per cent. of chlorine. Chlorine seems to act with most energy on those forms of carbon which are contaminated with hydrogen. The form in which it is combined is uncertain; nothing is extracted from the product by chloroform, benzene, alcohol, or ether.

Both lamp-black and charcoal absorb nitrogen when heated in a stream of that gas, and do not give it up on heating. The nitrogen exists probably in the form of cyanogen, since that substance is absorbed readily by charcoal at a red heat, yielding a product which, like those obtained by the direct action of nitrogen, yields ammonia when heated in a current of steam. Charcoal also absorbs nitrogen from nitrous and nitric oxides. Animal charcoal, albumin, and uric acid all leave a highly nitrogenous residue when ignited in a closed vessel.

Charcoal absorbs sulphur when heated to a red heat in sulphur vapour or carbon bisulphide. The sulphur is entirely removed by hydrogen, and is practically given up at a red heat. Filter paper soaked in carbon bisulphide and heated in sulphur vapour absorbs nearly its own weight of the latter. The compound so formed does not yield sulphur to carbon bisulphide or boiling aqueous potash.

Hard charcoal requires to be heated to a very high temperature before it will burn in dry oxygen.

JN. W.

Action of Aqua Regia on Carbon Bisulphide. By SCHLAGDEN-HAUFFEN and BLOCH (*J. Pharm.* [5], **28**, 241—242).—Excess of aqua regia is distilled with carbon bisulphide either immediately after mixing or after contact for some hours. Red nitrous fumes and unattacked carbon bisulphide first pass over, followed by a very volatile substance, which can be condensed by using a freezing mixture of ice and salt; it proves to be the trichloromethylsulphurous chloride of Kolbe, $SO(OCCl_3)Cl$; it is more readily prepared by this method than by Kolbe's process. The acid residue contains sulphuric acid.

W. T.

Molecular Weight of Potassium Persulphate. By G. BREDIG (*Zeit. physikal. Chem.*, **12**, 230—233).—Whilst freezing point experiments indicated $K_2S_2O_8$ as representing the molecule of potassium persulphate, the electrical conductivity gave numbers nearly agreeing with those obtained by Ostwald for potassium perchlorate, which is represented by the molecular formula $KClO_4$. The author points out that Ostwald's determinations were somewhat inaccurate, and that the conductivity experiments also correspond with the formula $K_2S_2O_8$.

J. W.

Double Halogen Compounds of Arsenic with Cæsium and Rubidium; Compounds of Arsenic Trioxide with the Cæsium, Rubidium, and Potassium Haloids. By H. L. WHEELER (*Amer. J. Sci.*, [3], **46**, 88—98).—The author has described the chemical properties and crystallographic condition of 12 new arsenical compounds containing a halogen and also cæsium or rubidium, of the types $3RbCl, 2AsCl_3$ and $RbCl, As_2O_3$. A potassium compound of the formula As_2O_3, KI has also been obtained.

These double haloid salts are prepared by dissolving arsenic trioxide in strong hydrochloric, hydriodic, or hydrobromic acid, and adding the required proportion of the metallic haloids, also dissolved in one of the said acids. Excess of one or the other of the constituents has, however, no effect on the composition of the product obtained. The double salts gradually crystallise out.

The oxy-compounds are obtained by making use of but very weak acid solutions. As might be expected, they are also formed by moistening the double haloids with water. Strong haloid acids reconvert them into double haloids.

L. DE K.

Incomplete Oxidation of Aluminium. By PIONCHON (*Compt. rend.*, **117**, 328—330).—When aluminium is heated in the flame of an oxyhydrogen blowpipe supplied with comparatively little oxygen, it burns brilliantly, and is converted into a dark grey powder which dissolves in hydrochloric acid with evolution of hydrogen and formation of aluminium chloride, whilst a residue of aluminium oxide is left. Estimations of the volume of hydrogen evolved, the quantity of aluminium chloride formed, and the weight of the insoluble residue show that the greyish product of the regulated combustion of aluminium in the oxyhydrogen blowpipe consists of a new oxide of aluminium mixed with small quantities of unoxidised metal and alumina. The new oxide has the composition Al_6O_7 or $Al_2O, 3Al_2O_3$.

C. H. B.

Note.—In his presidential address to the Chemical Section of the British Association at Nottingham, Emerson Reynolds pointed out that analytical and other data indicate the probable presence of partially oxidised aluminium in certain silicates.

C. H. B.

Isomorphism amongst Anhydrous Alums. By T. KLOBB (*Compt. rend.*, **117**, 311—314).—When chromium oxide, chloride, or sulphate is fused with ammonium sulphate, the double sulphate $Cr_2(SO_4)_3, 3(NH_4)_2SO_4$ is first formed, and crystallises in pale green,

microscopic, acicular prisms, which become rose-coloured when heated. It is insoluble in cold water, and is but slightly attacked by boiling water and dilute acids and alkalis. It remains unaltered at 350° , but at a red heat it decomposes, and a residue of chromic oxide is left.

If the fusion with ammonium sulphate is prolonged, anhydrous chromium ammonium alum is obtained in pale green, microscopic, hexagonal plates, which are not affected by boiling water, acids, or alkalis. A boiling solution of potassium hydroxide of sp. gr. 1.3 dissolves the salt very slowly. Water containing chromous chloride or stannous chloride does not dissolve it. At 350° , the salt becomes rose coloured without any change of composition, but at a bright red heat it is completely decomposed.

When chromium potassium alum is fused with ammonium sulphate, a mixed alum, $\text{Cr}_2(\text{SO}_4)_3, \text{SO}_4(\text{K}, \text{NH}_4)_2$, is obtained, isomorphous with the preceding compound.

If an excess of potassium sulphate is added, a salt of the composition $\text{Cr}_2(\text{SO}_4)_3, 3\text{K}_2\text{SO}_4$ is obtained in long, silky, green needles.

Another mixed alum, $\text{Cr}_2(\text{SO}_4)_3, (\text{NH}_4, \text{Na})_2\text{SO}_4$, isomorphous with the other two, is obtained by fusing chromium and sodium sulphates with ammonium sulphate.

Lachaud and Lepierre have already described the compounds $\text{Fe}_2(\text{SO}_4)_3, 3(\text{NH}_4)_2\text{SO}_4$ and $\text{Fe}_2(\text{SO}_4)_3, (\text{NH}_4)_2\text{SO}_4$. The former crystallises in prisms, and the latter in hexagonal tables. They differ from the corresponding chromium compounds in being readily attacked by cold water.

By operating in the manner described, it is easy to obtain anhydrous mixed alums of the following types, $(\text{Cr}, \text{Fe})_2(\text{SO}_4)_3, (\text{NH}_4)_2\text{SO}_4$; $(\text{Cr}, \text{Al})_2(\text{SO}_4)_3, (\text{NH}_4)_2\text{SO}_4$; and $(\text{Al}, \text{Fe})_2(\text{SO}_4)_3, (\text{NH}_4)_2\text{SO}_4$. Anhydrous aluminium alum can also be produced, but is difficult to isolate.

All these alums crystallise in hexagonal prisms, and their isomorphism affords further proof of the isomorphism of Al_2O_3 , Cr_2O_3 , and Fe_2O_3 on the one hand, and of K_2O , Na_2O , and $(\text{NH}_4)_2\text{O}$ on the other.

C. H. B.

Ferric Phosphate. By E. A. SCHNEIDER (*Zeit. anorg. Chem.*, 5, 84—87).—A solution of ferric chloride was saturated with normal calcium orthophosphate, and the solution dialysed. When the diffusate contained no more chlorine, the ferric phosphate on the dialyser set to a jelly containing ferric oxide and phosphoric anhydride, in the proportion 52.99 per cent. : 47.01 per cent. This hydrogel dissolves in ammonia with a reddish-brown colour, and by dialysing the solution ammonium phosphate is gradually removed. When the hydrogel is treated with potash, the resulting ferric hydroxide retains only 1.25 per cent. of phosphoric acid.

Ferric phosphate dissolves to a considerable extent in a solution of ammonium humate (containing 2.72 grams of ammonia per litre); after five months' digestion, 2 litres of such a solution were found to contain 9.144 grams of ash consisting of Fe_2O_3 , 52.21 per cent.; P_2O_5 , 45.42 per cent.; and SiO_2 , 2.00 per cent. The solubility of ferric phosphate in ferric sulphate is already known.

In concluding, the author points out that the ill effect of reversion in a mineral superphosphate may be much annulled in the soil if ammonium humate be present.

A. G. B.

Atomic Weights of Nickel and Cobalt. By C. WINKLER (*Zeit. anorg. Chem.*, **4**, 462—464).—The author suspected that the value lately obtained by him (this vol., ii, 469) for the atomic weight of cobalt might be somewhat too high, owing to the formation of a basic cobalt salt during the determination. He has therefore again determined this atomic weight by causing electrolytically deposited cobalt to act on silver sulphate; silver is then precipitated, and a relation between the equivalents of the two metals obtained. A trace of cobalt is retained by the silver, and may be afterwards estimated and allowed for. Two determinations gave $\text{Co} = 59.6356$ and 59.6164 ($\text{Ag} = 107.66$); these numbers are in close agreement with those previously obtained, so that the author's fears as to the accuracy of the method employed are groundless.

W. J. P.

Crystalline Chromium Tungstate. By E. F. SMITH and H. L. DIECK (*Zeit. anorg. Chem.*, **5**, 13—14).—The compound $\text{Cr}_2\text{O}_3 \cdot 5\text{WO}_3$ is obtained in the form of brown, orthorhombic needles, when equivalent quantities of potassium dichromate and tungstic acid are heated together until the mixture fuses and no more gas is evolved. The crystals are not attacked by aqua regia; they were decomposed for analysis by fusion with sodium carbonate and potassium nitrate.

A. G. B.

Action of Gases on Molybdenum and Tungsten. By E. F. SMITH and V. OBERHOLTZER (*Zeit. anorg. Chem.*, **5**, 63—68).—Carbonic oxide and ammonia were found to be without action on these metals at temperatures up to a red heat.

When molybdenum is heated at $150\text{--}200^\circ$ in carbonyl chloride, a liquid sublimate is formed, which solidifies to a reddish-brown, gelatinous mass melting below 100° . The analysis of this product indicates that it is a mixture in equal molecular proportions of MoOCl_4 and $\text{Mo}(\text{CO})\text{Cl}_4$.

A similar treatment of tungsten gives rise to an orange-red sublimate consisting of the oxychloride, WOCl_4 , and containing carbon, which is left when the oxychloride is resublimed.

A reddish-brown, amorphous sublimate of the formula $\text{Mo}_5\text{S}_8\text{Cl}_9$ was obtained by heating molybdenum to a red heat in sulphur chloride. Tungsten, under similar conditions, yields a red, crystalline sublimate, which is unstable in air, and has the formula $\text{W}_2\text{S}_7\text{Cl}_8$, being regarded by the authors as a compound of $\text{W}_2\text{S}_3\text{Cl}_4$ with $2\text{S}_2\text{Cl}_2$.

A. G. B.

Complex Inorganic Acids. By F. KEHRMANN (*Zeit. anorg. Chem.*, **4**, 465—466).—A polemical paper dealing with Friedheim's criticism (this vol., ii, 472) of the author's work (*ibid.*).

W. J. P.

Sulphur Compounds of Thorium. By G. KRÜSS and C. VOLK (*Zeit. anorg. Chem.*, **5**, 75—79).—Neither by heating potassium thorium chloride in hydrogen sulphide, nor by heating thorium oxide

in carbon bisulphide in the manner adopted by Chydenius, could the authors obtain the compounds ThS_2 and $\text{Th}_3\text{O}_4\text{S}_2$, which Chydenius claims to have prepared (*Jahresber.*, 1863, 194). In both cases, the compound produced contains thorium and sulphur in equal atomic proportions, indicating the existence of ThS or ThOS .

A. G. B.

Variety of Gold Purple Soluble in Water. By E. A. SCHNEIDER (*Zeit. anorg. Chem.*, 5, 80—83).—To obtain a solution of this form of gold, an alloy of gold, tin, and silver is treated with concentrated nitric acid, and the resulting black powder is washed with ammonia, whereby a ruby-red coloured solution is obtained. This solution is dialysed until it contains no more ammonia; it is coagulated by dilute acids and salts, and by heating under pressure, but not by alcohol, nor by concentrated sulphuric acid. It contains 0.5800 gram of gold, and 5.4048 grams of stannic oxide per litre; 50 c.c. of the solution gelatinises when evaporated to 3 c.c., but the jelly dissolves again in water. Diluted 10 times, it is still red, and a layer 1 cm. thick allows the red, yellow, and less refrangible rays of the green in the spectrum to pass. Potassium cyanide decolorises the liquid, and causes the separation of stannic acid. When shaken with mercury, the colour of the liquid passes into brownish-red, and the mercury extracts gold. When poured into an excess of strong hydrochloric acid, the solution changes in colour to violet, and yields finely-divided gold on dialysis. This behaviour indicates that the soluble form of purple gold is a mixture of the hydrosols of gold and stannic acid, a conclusion supported by the fact that the addition of a few drops of gold chloride and a reducing agent to the hydrosol of stannic acid produce a purple solution. The presence of the hydrosol of stannic acid is essential to the existence of the hydrosol of gold. The author notes a similar behaviour of silver chloride, which can be obtained in a condition in which it can only be coagulated by acids when silver nitrate is added to a dilute solution of ferric chloride.

The hydrosol of stannic acid is best obtained by pouring a dilute solution of stannic chloride into a very dilute solution of ammonia, and dialysing. The clear liquid contains 5.164 grams of stannic oxide per litre. Its behaviour is similar to that of the purple gold solution described above.

A. G. B.

Mineralogical Chemistry.

Rock Salt from Deésakna. By J. LOCZKA (*Zeit. Kryst. Min.*, 22, 82; from *Földtani Közlöny*, 21, 353—358).—Deésakna is situated in the Hungarian county of Szolnok-Doboka, and the salt mined at this locality is characterised by its extreme purity. The author subjected to analysis a pure, transparent crystal of sp. gr. 2.148 with the following results.

Na.	Cl.	H ₂ O.	Total.
39.41	60.64	0.02	100.07

B. H. B.

Falkenhaynite, a new Mineral of the Wittichenite Group. By R. SCHARIZER (*Zeit. Kryst. Min.*, 22, 85; from *Jahrb. d. k.k. Geol. Reichsanst.*, 40, 433).—A greyish-black, dense ore from Joachims-thal was analysed, and, after deduction of 13.16 per cent. of quartz, 12.77 per cent. of magnesia-bearing spathic iron ore, and 3.66 per cent. of copper pyrites, gave results corresponding with the formula $\text{Sb}_2\text{S}_3\text{Cu}_6$, in which one-quarter of the antimony is replaced by arsenic, and one-fifth of the copper by iron and zinc in the ratio of 5 to 3.

B. H. B.

Franckeite, a new Ore from Bolivia. By A. W. STELZNER (*Jahrb. f. Min.*, 1893, ii, Mem. 114—124).—The ore described occurs in the Animas mining district, south-east of Chocaya. Locally it is known as *llicteria*, and is described by Jackowski, a Polish engineer resident in the district, as a mineral unknown in Europe, and as consisting of lead, zinc, tin, and silver. Analysis (by C. Winkler) yielded the following results.

Pb.	Sn.	Sb.	S.	Fe.	Zn.	Gangue.	Total.
50.57	12.34	10.51	21.04	2.48	1.22	0.71	98.87

The mineral also contains about 0.1 per cent. of germanium and 1 per cent. of silver. The formula is $5\text{PbS}, 2\text{SnS}_2, \text{Sb}_2\text{S}_3$. This new mineral, which is of special interest as indicating the character of the occurrence of tin in the Bolivian mines, and also as containing germanium, is named *franckeite* by the author in honour of C. and E. Francke, two mining engineers specially interested in Bolivian mining.

B. H. B.

Kylindrite. By A. FRENZEL (*Jahrb. f. Min.*, 1893, ii, Mem. 125—128).—At the Santa Cruz mine at Poopó, in Bolivia, a new mineral has been discovered. This the author has named *kylindrite* from the cylindrical form in which it occurs. The mineral has a metallic lustre, a blackish-grey colour, a hardness of 2.5 to 3, and a sp. gr. 5.42. Analysis gave the following results.

Pb.	Ag.	Fe.	Sb.	Sn.	S.	Total.
35.41	0.62	3.00	8.73	26.37	24.50	98.63

The formula is therefore $\text{Pb}_6\text{Sb}_2, \text{Sn}_6\text{S}_{21}$ or $6\text{PbS}, \text{Sb}_2\text{S}_3, 6\text{SnS}_2$. The mineral differs both in chemical composition and in physical properties from the two similar sulphur lead salts of tin and antimony, plumbostannite and *franckeite*.

B. H. B.

Artificial Minerals obtained in Chemical Industries. By C. WINKLER (*Zeit. angew. Chem.*, 1893, 445—447).—The author describes the occurrence of the following minerals produced artificially.

1. *Iron pyrites*, obtained in the process of recovering sulphur from soda residues. The mineral is cryptocrystalline, and has a sp. gr. of 4.7336. Its composition is as follows.

Fe.	S.	Residue.	Total.
46·33	52·52	1·86	100·71

2. *Gypsum*, obtained in the same process. It occurs in well-developed monoclinic crystals, yielding, on analysis,

CaO.	SO ₃ .	H ₂ O.	Total.
32·09	46·56	21·07	99·72

3. *Trona*, obtained in the manufacture of bicarbonate of soda by the ammonia-soda process. It is formed in magnificent, pellucid, monoclinic crystals. As formed in the Ebensee ammonia-soda works, the product has exactly the same composition as natural trona, according to B. Reinitzer, $\text{Na}_3\text{H}_2(\text{CO}_3)_3 + 3\text{H}_2\text{O}$. The author's analysis leads to the formula $\text{Na}_3\text{H}(\text{CO}_3)_2 + 2\text{H}_2\text{O}$. B. H. B.

New Natural Phosphates. By A. GAUTIER (*Compt. rend.*, 116, 1171—1177).—In a previous paper (this vol., ii, 419), the author pointed out that the bed of concretionary phosphates found in the grotto of Minerva constitutes a new type of phosphorites in which the phosphoric acid is combined with calcium and aluminium. This remarkable deposit furnishes also the bibasic natural calcium phosphate, *brushite*, and a new aluminium phosphate.

Brushite, $\text{PO}_4\text{CaH}_2\text{2H}_2\text{O}$, has hitherto been found only in a guano rock in the Antilles. The description given by Dana of metabrushite corresponds exactly with the properties of the Minerva brushite. The analyses given by the author are in accord with the formula $2\text{PO}_4\text{CaH}_2 + 3\text{H}_2\text{O}$.

Minervite is the name given by the author to the new aluminium phosphate. Its composition, $\text{P}_2\text{O}_5, \text{Al}_2\text{O}_3, 7\text{H}_2\text{O}$, approaches that of callainite and gibbsite. B. H. B.

Chondrostibian, a new Swedish Mineral. By L. J. IGELSTRÖM (*Zeit. Kryst. Min.*, 22, 43—46).—In January, 1893, the author discovered another new antimony mineral in the Sjö mine, celebrated for its occurrence of the minerals hæmatostibiite, ferrostibian, stibiate, basiliite, and melanostibian. To this new mineral the author has given the name of "chondrostibian" (*χόνδρος*, a grain, and *stibium*, antimony). The small grains of the mineral occur in barytes, and appear at times to form minute crystals of octahedral form. On analysis, it gave the following results.

Sb ₂ O ₅ .	As ₂ O ₅ .	Mn ₂ O ₃ .	Fe ₂ O ₃ .	H ₂ O.	Total.
30·66	2·10	33·13	15·10	19·01	100·00

The formula is consequently $3\text{R}_2\text{O}_3, \text{Sb}_2\text{O}_5 + 10\text{H}_2\text{O}$, in which R_2O_3 represents Mn_2O_3 and Fe_2O_3 . B. H. B.

Descloizite from the Obir. By A. BRUNLECHNER (*Jahrb. f. Min.*, 1893, ii, Ref. 254—255; from *Carinthia*, 2, 8).—The crystals of descloizite were found in fissures in limestone, associated with goethite. Pseudomorphs of descloizite after vanadinite are also met with. The

results of analysis of these are given by the author. The minerals originally occurring in the fissures were galena, blende, marcasite, and calcite. Subsequently the galena became converted into lead sulphate by the decomposition of the marcasite, the lead sulphate was then converted into vanadinite, and finally desloizite was formed.

B. H. B.

Ettringite and Alabandine from Arizona. By A. J. MOSES (*Zeit. Kryst. Min.*, 22, 16—19).—*Ettringite*, $H_{18}Ca_6Al_2O_{18}(SO_4)_3 + 24H_2O$.—This mineral was found at the Lucky Cuss mine at Tombstone, Arizona, in white, crystalline limestone incrusting fissures and cavities in a silicate of lime and alumina. It resembles a finely fibrous pectolite. Its hardness is somewhat above 2, and its sp. gr. 1.27.

Alabandine.—A deposit of alabandine was found at the same mine. The quantity raised amounted to 50 tons. On analysis, the mineral yielded 36.90 per cent. of sulphur and 63.03 per cent. of manganese. Its colour is dark steel-grey to deep black with an olive-green streak. Its hardness is 3 to 4, and its sp. gr. 4.03.

B. H. B.

Idocrase. By F. PISANI (*Jahrb. f. Min.*, 1893, ii, Ref. 252; from *Bull. Soc. fran. min.*, 15, 47—49).—The author gives the following results of an analysis of idocrase from the Septimer.

SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	MgO.	CaO.	Loss on ignition.	Total.
39.0	1.8	14.3	6.7	37.4	0.9	100.1

The mineral forms compact, pale greenish-yellow, laminated masses, having a hardness of 6.5 and a sp. gr. of 3.28.

B. H. B.

Peculiar Lava from Northern California. By J. S. DILLER (*Jahrb. f. Min.*, 1893, ii, Ref. 338—339; from *Bull. U.S. Geol. Surv.*, 79, 33).—The author describes a late volcanic eruption in Northern California and its peculiar lava. In the latter, the pyroxene is chiefly hypersthene, monoclinic augite being of rarer occurrence. Scattered through the mass are quartz, felspar, and olivine, and in the ground-mass there is a second generation of felspar with globulitic glass. The lava has the following composition.

TiO ₂ +									
SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
79.49	11.60	0.33	0.49	1.64	0.09	1.52	4.04	0.68	99.88

B. H. B.

Two Turkish Meteorites. By S. MEUNIER (*Compt. rend.*, 117, 257—258).—The author has examined specimens of the meteorites recently presented to the Museum of Natural History by Halid Edhem Bey. The first was found in 1873 at Tirnowa, in Roumelia. It is covered with a black crust about a millimetre in thickness. On fracture, a clear, grey mass is presented, characterised by its clastic or fragmentary structure. Its sp. gr. is 3.69. The meteorite belongs to the lithological type designated since 1870 in the Museum collection by the name of *mesminite*.

The second meteorite fell on June 2, 1883, in a forest near the village of Urba. It is uniformly white. It has a sp. gr. of 3.427, and is very finely granular. B. H. B.

Analysis of the Wawilowka Meteorite. By P. MELIKOFF (*Ber.*, 26, 1929—1932).—This meteorite fell in June, 1876, at Wawilowka, in the Cherson district. In 100 parts it contains:—

A, decomposed by hydrochloric acid, Fe, 1.79; Ni, 0.93; Co, 0.06; FeS, 6.82; P_2O_5 , 0.21; olivine, 55.08.

B, undecomposed by hydrochloric acid, FeO, Cr_2O_3 , 0.23; silicate, 34.27.

The metallic iron and nickel are present nearly in the ratio $NiFe_2$; the olivine has the composition $2Fe_2SiO_4, 5Mg_2SiO_4$, with some of the Mg and Fe replaced respectively by Ca, K, Na, and Mn; and the undecomposable silicate belongs to the class $M'SiO_3$. C. F. B.

New Iodine Spring in Austrian Silesia. By M. GLÄSER and W. KALMANN (*Zeit. angew. Chem.*, 1893, 447—448).—The authors have analysed the water from a salt spring at Roy, in Austrian Silesia, with the following results, expressed in grams per litre:—

CO_2	SiO_2	Cl.	Br.	I.	SO_3	FeO.
0.0885	0.0122	15.1236	0.1025	0.0383	0.0031	0.0285
CaO.	MgO.	Na_2O .	K_2O .	Organic.	Fixed residue.	
0.9487	0.4661	11.4684	0.1772	0.1028	25.5080	

The sp. gr. at 15° is 1.01809.

B. H. B.

Physiological Chemistry.

Exercise and Respiratory Interchange. By W. MARCET (*Proc. Roy. Soc.*, 54, 42—52).—In three persons, if the excretion of carbonic anhydride fell, the oxygen absorbed rose, and *vice versa*. In a fourth person, of immature age, the oxygen absorbed and the carbonic anhydride expired rose and fell together.

During exercise (stepping), at first there is an accumulation of carbonic anhydride in the blood; this is next given out in the form of a wave, which is renewed after a certain lapse of time. In two persons, the ratio of carbonic anhydride expired in rest to that expired during exercise was found to be the same, namely, 0.123; but further experiment is necessary before this can be laid down as a general law. As a rule, half an hour's rest was sufficient to bring matters back to the normal condition. W. D. H.

Influence of Sodium Chloride on the Digestibility and Assimilation of Protein. By S. GABRIEL (*Zeit. Biol.*, 29, 554—569).—Former experimental work has led to the conclusion that

sodium chloride, like water, is of great use to the organism in promoting digestion and the metabolic phenomena that follow absorption. The present experiments, made on three sheep, are divided into periods during which salt was and was not given. The differences of the numbers in the two periods, although not very striking, yet tend to prove the conclusion just alluded to. W. D. H.

Effect of Salt on Digestion. By E. v. WOLFF and J. EISENLOHE (*Exper. Stat. Record*, 4, 974—976; from *Landw. Jahrb.*, 22, 605—627).—Stutzer's experiments with artificial digestive fluids on proteids showed a higher rate of digestibility in presence of salt than without salt.

Experiments were made in which sheep were fed with (1) hay alone; (2) hay and brewer's grains; (3) hay and field beans. Each experiment comprised three periods: the first without salt, the second with 4 grams, and the third with 8 grams of salt in the food of each sheep. Besides determining the coefficient for the protein by the difference between the amounts eaten and excreted, the metabolic nitrogen was determined in the fresh fæces with acid pepsin solution, and in the air-dry fæces with both pepsin and pancreas solutions. The digestibility of each ration was determined by Stutzer's method. The results failed to show any increase in amounts digested in presence of salt. Experiments with a horse gave similar results.

There is, however, no doubt that salt has a good effect on the general condition of animals and, in some cases, on digestion; as, for instance, when there is a deficiency of hydrochloric acid in the digestive juice. N. H. M.

Digestibility of Milk and Bread. By A. MAGNUS-LEVY (*Pflüger's Archiv*, 53, 544—560).—The experiments carried out on L. Zuntz, æt. 16, consisted in analysing the diet (milk, and then milk with bread and butter) and the excreta. This simple diet appears to be very well used, and the loss by putrefaction is insignificant. Bunge states that those who do not take alcohol make better use of their food than others. The subject of the present experiments was an abstainer, and the results do not altogether confirm Bunge's statement, although they are not very conclusive. W. D. H.

Influence of Light on Metabolic Processes. By L. GRAFFENBERGER (*Pflüger's Archiv*, 53, 238—280).—The principal change produced in animals by the absence of light is an accumulation of fat. This, however, is not strictly proportional to the duration of the darkness.

The assimilation of nitrogen, the digestion coefficient, the formation of liver glycogen, and the relation of water to solids in the body are not affected.

The only other results of darkness noted were a lessening of the quantity of blood and of hæmoglobin, and, if the deprivation of light were very prolonged, the development of bony tissue and of the liver was delayed. In developing animals, the heart and muscular tissues were relatively heavier under the influence of darkness.

W. D. H.

Urea in the Blood of Birds. By A. GARROD (*Proc. Roy. Soc.*, **53**, 478—484).—Urea occurs in birds' blood in quantity approximately equal to that in mammalian blood. The author has previously insisted that the kidneys, not the liver and spleen, form the situation where uric acid is formed. He considers that the discovery of urea in birds' blood, and the absence of uric acid there, lends support to this contention. If so, nitrogenous metabolism is practically identical in both birds and mammals: in mammals, the urea leaves the body as such; in birds, synthetic processes in the kidney lead to its conversion into ammonium urate, in which form it is excreted. W. D. H.

Diastatic Ferment in Blood. By M. BIAL (*Pflüger's Archiv*, **53**, 156—170).—The saccharifying power of human blood is less than that of some other animals. The products are dextrin and dextrose. The blood has also the power of changing maltose into dextrose. In the new-born child, the saccharifying power is weak or absent, and the same is true also for newly born lower animals. W. D. H.

Glycogen. By W. SAAKE (*Zeit. Biol.*, **29**, 429—483).—The observation of Langley and others, that glycogen occurs in the body in the presence of some vehicle of proteid-like nature, is confirmed by microchemical investigation of various glycogen-containing cells of adult and foetal organs. The comparison of hæmoglobin in its vehicle, the stroma, is made. The vehicle, however, is not ordinary albumin, for although it is coagulated by alcohol, it swells in water without dissolving, and is not coagulated by trichloroacetic acid.

Fraenkel's method for the preparation of glycogen is criticised; and still more so are his views that the glycogen is actually in combination with proteid in the body. Mechanical admixture is considered sufficient to explain all his conclusions. W. D. H.

Absorption from the Stomach. By J. BRANDL (*Zeit. Biol.*, **29**, 277—307).—Tappeiner (*ibid.*, **16**, 497) obstructed the pylorus in dogs by a bladder inserted through a fistula, and found that an aqueous solution of chloral hydrate did not produce narcosis. If, however, the surface of a small amount of the duodenum were allowed to have absorptive play also, narcosis soon set in. An alcoholic solution of the same substance was, however, rapidly absorbed by the stomach, and produced the usual narcosis. Quantitative experiments with sugar solutions showed that the stomach has little or no absorptive power for aqueous solutions, whilst the presence of alcohol increases its absorptive activity. v. Anrep (*Du Bois Reymond's Archiv, Physiol. Abth.*, 1881, 504) found the absorption in the stomach greater than Tappeiner stated. It is suggested, and the present experiments confirm the suggestion, that this is explained by the fact that he used solutions of greater concentration than Tappeiner did.

The present experiments, all made on one dog, relate to sugar, peptone, and sodium iodide; in all cases increase of concentration led to a stimulation of the process of absorption, and the consequent disappearance from the stomach of a larger amount of material. In all cases also the presence of the solution led to a large secretion from

the gastric walls, usually in excess of the fluid administered. This still further diluted the substance, which, nevertheless, is readily absorbed by the intestinal wall, where there is no necessity for great concentration in order that absorption may occur.

Further, all these effects are increased by alcohol. Alcohol does not stand alone here, but other stomachic stimulants, such as sodium chloride, mustard oil, pepper, oil of peppermint, and orexine hydrochloride act similarly. Bitters do not produce the effect. The presence of colloïd substances, like starch and gum, enormously diminishes the absorption: W. D. H.

Secretion and Absorption in the Small Intestine. By F. VOIT (*Zeit. Biol.*, 29, 325—397).—The experiments were made on dogs, and the first series confirm the observation of Herrmann that isolated loops of intestine contain after a time fæcal-like masses derived in large measure from the secretion of the intestinal wall. On an ordinary diet also very largely, and on a flesh diet almost exclusively, are the fæces passed of similar origin. The same occurs during hunger, and food only slightly increases the amount of fæces passed. The large digestive glands (liver and pancreas) have scarcely any part in the process. By giving large quantities of flesh, the nitrogen in the fæces is increased; but here, again, it is not the nitrogen of undigested food, but an increase in the nitrogen of the intestinal juice. The ash, however, of flesh is not so well absorbed if given in large amounts. The fæces of hunger contain not unimportant quantities of fat (compare "Physiology of Starvation," this vol., ii, 477).

The second series of experiments relates to the absorption of calcium salts. The greater part of these salts, after a diet containing them in large quantity, comes from the food direct. Comparison with the fæces of hunger shows that a certain amount also is secreted in the intestinal juice, but this is only very slightly increased by food rich in lime. The bile plays here only an insignificant part. Another part of the absorbed calcium salts leaves the body in the urine. The amount of calcium salts absorbed is increased with difficulty by tricalcium phosphate, by milk or by injection of proteid-calcium combinations into the intestine. Injection of 1 to 3 per cent. solutions of calcium chloride are more efficacious, but are contra-indicated by the fact that they produce pathological changes in the mucous membrane.

The third and last series of observations relates to iron, which was given in the form of *liquor ferri albuminati*, oxyhæmoglobin, and ferric citrate. The absorption of these substances was found to be very low. The small quantities which appeared to be absorbed left the body partly in the urine, but chiefly in the intestinal juice. The bile hardly comes into account in this connection; the little iron it does contain appears to be absorbed by the intestinal wall. It is calculated that the small amount of iron absorbed leads only to an output in the intestine of a few milligrams daily. The greater part of the iron in the fæces comes directly from that administered.

W. D. H.

The Phosphates of Milk. By DUCLAUX (*Exper. Stat. Record*, 4, 978; from *Ann. Inst. Pasteur*, 1893, 2—17).—Phosphates exist in milk

in a soluble form, tricalcium phosphate and sodium phosphate, and in an insoluble form, phosphates of iron, aluminium, magnesium, and calcium. The insoluble portion contains about twice as much lime and calcium phosphate as the soluble portion.

"Phosphate milk," a milk in which the phosphates are supposed to have been increased by feeding calcium phosphate, contains no more phosphates than other milk. Analyses of milk from various sources showing the total lime as calcium phosphate, the excess of phosphoric acid, mostly combined with aluminium, iron, magnesium, and sodium, and the other mineral constituents are given. The different results agree closely, so that any addition of either soluble or insoluble phosphates could be detected from the change in the relation of soluble to suspended phosphates. N. H. M.

Effect of Work on the Excretion of Phosphoric acid. By F. KLUG and V. OLASAVSKY (*Exper. Stat. Record*, 4, 976; from *Arch. Ges. Physiol.*, 54, 21—26).—Preysz (*Ungar. Arch. Med.*, 1, 38) found that the phosphoric acid excreted by a man was increased by muscular work. The authors confirmed this with experiments on a dog. During 10 days of rest, the average daily amount of phosphoric acid excreted in the urine of the dog was 0.3175 gram. When put to hard work, the amount increased to 0.57 gram. On the next day, it fell to 0.28 gram. The increase is probably due, to a great extent, to the lactic acid formed in the muscles during work; perhaps, in a smaller measure, to carbonic anhydride. Water containing lactic or carbonic acid will dissolve much more phosphoric acid from fresh meat and bones than pure water. Moreover, by adding lactic acid to a dog's food, the phosphoric acid in the urine was distinctly increased.

N. H. M.

Transformations of Arsenious Anhydride in the Organism. By D. VITALI (*L'Orosi*, 16, 73—87; compare following abstract).—The author gives a summary of our knowledge concerning the changes undergone by arsenious anhydride in the organism. Neither arsenic acid nor arsenious acid combines with albumin to form albuminates. By experiments on dogs, the author confirms the observation that arsenious anhydride is converted by the organism into arsenic anhydride, which then passes into the urine; the arsenic acid is not found free in the urine; but in a state of combination, and probably displaces phosphoric acid in phosphoglyceric acid; the latter being a decomposition product of lecithin, it would seem that arsenic can replace phosphorus in this. This is confirmed by an examination of the liver and brain of a dog to which considerable quantities of arsenious anhydride had been administered. W. J. P.

Absorption and Physiological Action of Arsenic Trisulphide. By D. VITALI (*L'Orosi*, 16, 145—149).—Pure arsenic trisulphide is not poisonous; the commercial product, however, contains more or less arsenious anhydride, which is, of course, very poisonous. The administration of considerable quantities of the trisulphide to a dog is attended by an improvement in the health of the animal; the explanation of this lies in the fact that only a small proportion of the

sulphide passes into the urine as arsenic acid. The effect is hence the same as that of administering very small doses of the latter substance; this, as is known, is beneficial.

The author again confirms his conclusion (compare preceding abstract) as to the oxidation of arsenious anhydride in the animal organism. In searching for arsenic acid in the urine of the dog, magnesia mixture should be added, and the precipitated ammonium phosphate and arsenate reprecipitated from its acetic acid solution until colourless; on then applying Marsh's test, unmistakable evidence of the presence of arsenic acid is obtained. W. J. P.

Physiological Action of the Two Isomeric Ethylic Thio-carbamates. By W. J. SMITH (*Pflüger's Archiv*, **53**, 481—490).—These two isomerides differ in the position of the sulphur in the molecule. From experiments on dogs and frogs, it was found that practically none or only traces of either pass into the urine as such; a part of the sulphur is excreted as sulphuric acid. The nitrogen output is also increased. The symptoms produced are of the nature of paralysis followed by death; and the more poisonous of the two compounds was that in which the sulphur was combined as CS·OEt, not as CO·SEt. W. D. H.

Physiological Action of Organic Oximides. By H. W. POMFRET (*Proc. Roy. Soc.*, **53**, 398—404).—The action of fatty aldehydes on voluntary muscle is to produce contracture and loss of irritability; on nerves, a primary slight increase of irritability becomes more evident as the series is ascended; on the spinal cord, there is a primary increase, followed by a secondary depression; as a rule, vessels are constricted. All tend to slow the heart, but show a primary tonic action. As the atomic weight of the aldehyde increases, weaker solutions are required to show the tonic effect, and the arrest in diastole is more quickly reached. The corresponding aldoximes reflect the combined action of a nitrile and aldehyde, becoming more toxic as the series is ascended.

Aromatic aldehydes have the same type of action, but are more powerful, and the corresponding aldoximes scarcely differ at all from these.

Acetoxime and isonitrosoacetone, in their action, closely resemble the fatty aldoximes.

Acetone differs from the aldehydes chiefly in causing no contracture. Its effect on vessels and heart is very slight. The COH group is believed to be closely associated with contracture, a phenomenon stated to be due to irritation of the end plates. It is prevented by curare. Experiments on the oxidation of acetoxime and isonitrosoacetone led to the detection of an aldehyde (pyruvic aldehyde). If this occurs in the tissues, it will account for the contracture they produce. W. D. H.

Physiological Action of Sugar. By V. HARLEY (*J. Physiol.*, **15**, 139—161; *Proc. Roy. Soc.*, **54**, 179—186).—A full account of experiments previously recorded in brief (see this vol., ii, 543). W. D. H.

Physiological Action of Sugars. By M. CREMER (*Zeit. Biol.*, 29, 484—553).—The paper contains lengthy dissertations on the glycogen question, and on the properties of sugars, with references to literature. There are also experiments recorded on man and animals, relating to the question of whether glycogen originates from different kinds of sugar given by the mouth, and which of these passes into the urine. The most interesting facts appear to be those relating to the rarer forms of sugar. It is found that d-mannose works undoubtedly in increasing glycogen. It goes more readily into the urine than dextrose or levulose, but not so easily as the pentoses (arabinose, xylose, and rhamnose), or as sorbose. Galactose also appears to increase glycogen in the body. W. D. H.

Physiological Action of Uric acid. By A. HAIG (*J. Physiol.*, 15, 167—175).—Experiments on the author's own person have led him to the conclusion that uric acid, taken by the mouth, increases the excretion of that substance in the urine. W. D. H.

Physiological Action of Quinoline, Isoquinoline, and their Derivatives. By R. STOCKMAN (*J. Physiol.*, 15, 245—248).—Quinoline is a strong antiseptic and antipyretic, depressing the central nervous system. No difference, quantitative or qualitative, could be detected between its action and that of isoquinoline. The two methiodides also acted in precisely the same manner, causing a more paralyzing action on the motor nerves than the alkaloids themselves.

The physiological action of quinaldine (α -methylquinoline), lepidine (γ -methylquinoline), $\alpha\gamma$ -dimethylquinoline, orthotoluquinoline, and paratoluquinoline was also investigated.

Tartrate of quinaldine has, on frogs and rabbits, an action similar to that of quinoline, but is somewhat less active; the dimethyl compound is still less active. It would appear, therefore, that the substitution of methyl for hydrogen weakens the depressing action on the nervous system. The other substances act in every respect like quinaldine.

The position of the nitrogen atom or of the methyl group exerts no influence on the physiological action of these substances.

W. D. H.

Dandruff of the Horse. By F. SMITH (*J. Physiol.*, 15, 162—166).—Dandruff obtained by the grooming of horses consists of epithelium scales, fat, dirt, and hair, together with the secretion of the sebaceous glands. Analysis gave the following results.

Water.....	17.96	
Fat.....	12.40	
Organic matter....	56.22,	containing 1.08 urea
Ash.....	13.42	„ 2.45 silica

The fat resembles lanolin, and is increased by a diet of oats, as compared with one of hay. Cholesterol was obtained in a crystalline form from the organic matter; there is also proteid present. The ethereal or alcoholic extract is green, especially with a hay diet, and

this is lessened by a diet of oats. Spectroscopic examination of the fluid left little doubt that the green pigment is a derivative of chlorophyll, the proportion of which varies with that in the food. Hay contains the same derivative of chlorophyll, namely, phyllocyanin. The greatest amount of chlorophyll in the food leaves the body in the faeces. None was found in the blood.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Butyl Alcoholic Fermentation and the Butylic Ferment. By M. W. BEIJERINCK (*Rec. Trav. Chim.*, 12, 141—153; and *Verhand. Kon. Akad. Wetensch., Amsterdam*, 1893 [2e Sec.], Deel 1, No. 10).—Normal butyl alcohol is formed during the butyric fermentation of sugar, and also by a fermentation named by the author butylic; it is also found as an accessory product of the assimilation of two other microbes occurring in the soil. That which was believed by Fitz (Abstr., 1882, 1121) to be the butylic fermentation is, in reality, only the butyric fermentation. The two ferments resemble one another, and both belong to a new species of *Granulobacter*, so-called because they contain granulose. *Granulobacter butylicum*, the true butylic ferment, occurs in association with Fitz's ferment, *G. saccharobutyricum*, on the surface of corn grains. The author has, however, found *G. butylicum* alone on certain hulled grains, *Hordeum distichon nudum* and *Hordeum vulgare himalayense*. To study the ferment, these grains are to be recommended, but they must be collected during the summer of the same year. About 20 grams are ground, and the flour made into a paste with 100 c.c. of hot water, so that the temperature of the paste is not higher than 95°, a precaution which it is necessary to observe, as the spores of the butylic ferment are killed by keeping them for a few seconds at 100°. The other organisms are destroyed below 95°. Fermentation is allowed to proceed at 35°; at the end of 48 hours the starch liquefies, gas is evolved, and the odour of butyl alcohol becomes apparent; there are, however, present in this liquid foreign bacteria, whose spores have survived the high temperature, notably the forms known as *Bacillus subtilis*; these have, however, no ill effect on the butylic ferment, which is anaërobic, and grows in the lower portion of the culture liquid. In the event of contamination with the butyric ferment (also anaërobic), the butyl fermentation is arrested. From the crude fermentation, pure cultures are then made in sterilised, faintly acid wort, contained in vessels which can be filled and inoculated without the admission of air; the dissolved atmospheric oxygen is previously removed from the wort by boiling. The fermentation is conducted at 35°, and lasts about 60 hours. The yield of butyl alcohol is about 1—2 per cent. of the flour employed, and the other products of the fermentation are carbonic anhydride and hydrogen; volatile organic acids are quite absent, which dis-

tinguishes it from the butyric ferment. The organism can be precipitated from the liquid by means of ethyl alcohol, the latter being added until the mixture contains 70 per cent. of it; after being dried in the air, the ferment forms a brown, pulverulent substance, which is coloured blue by iodine, and contains about 15 per cent. of water, and (dried at 110°) 25 per cent. of proteid substances. Preparations have been kept for six years without losing their vitality. The dried, as well as the fresh, organism contains an enzyme "*amylase*," similar to the diastase of malt, the presence of which can be readily demonstrated by its hydrolytic action on starch, maltose, and dextrin, but no glucose is formed. The "*amylase*" is secreted only on the surface of the bacteria, but they deposit a variable quantity of granulose within the cell. The organism is treated with cold concentrated hydrochloric acid, washed, neutralised, and the granulose, extracted by means of boiling water, is precipitated by alcohol. It seems to be identical with that obtained from potatoes, as it is transformed by the above described "*amylase*" into maltose and dextrin, and by the maltase of non-germinated grain into erythrodextrin and maltose.

It has been observed that the spores of the butylic bacteria only retain their vitality for three months in the fermented liquids, whilst the bacteria themselves die earlier; the granulose then disappears, which is, doubtless, due to the *amylase*, as this penetrates the cells of the dead organisms and saccharifies the granulose. The bacteria are, therefore, best preserved in the dry state. The fermentation and propagation of the organism are only possible in the entire absence of oxygen, or when the pressure of this gas is reduced to an extremely small minimum. In the former case, a variety of the organism results which is denoted by the author the "*clostridium form*"; and in the latter case, a variety denoted the "*oxygen form*." The "*oxygen form*" is not easily distinguishable from the *Bacillus subtilis*, is very mobile, and is coloured yellowish-brown, like most bacteria, by iodine; hence it does not contain granulose. If the quantity of oxygen is relatively large, the mobility ceases, and the bacteria becomes more or less filiform; finally, when the pressure of oxygen exceeds the maximum limit, all multiplication and fermentation is arrested.

The butylic fermentation always commences with a period in which the "*oxygen form*" predominates; the composition of the evolved gas is $\text{CO}_2 + 4\text{H}_2$. After the last trace of oxygen has disappeared, and the "*clostridium form*" appears, the development of hydrogen diminishes and that of the carbonic anhydride increases, until, at the end of the fermentation, the composition of the evolved gas is $5\text{CO}_2 + \text{H}_2$. The principal phase in this fermentation is characterised by the predominance of the *clostridium form*. The spindles have at one extremity an ellipsoidal cavity, enclosing a spore of the same shape. These spores may be heated for some seconds at 100° without losing their vitality. It is, also, at this stage of the fermentation that the granulose accumulates and the secretion of the "*amylase*" is most active. The author believes that the obligatory and optional anaërobic fermentation depends on the presence of easily reducible substances; when these fail, life is impossible or possible

only under specially favourable conditions of nutrition and in presence of oxygen under low pressure. The anaërobic cultures of the ferment are best obtained at a temperature of 10—15° with solutions of glucose or starch in water, to which 0.05 per cent. of the potassium hydrogen phosphate and 1 per cent. of peptone have been added.

The third form of the anaërobic fermentation, designated by the author "*temporary anaërobiose*," and which occurs in ordinary alcoholic fermentation, is characterised by the necessity of renewing the free oxygen after the multiplication of a small number of cells (20—30 in the case of yeast), and, doubtless, depends solely on a reserve of this element in the protoplasm of the cell. This last circumstance explains, to a certain degree, why the reducing function, which is never wanting in any obligatory or optional anaërobic fermentation, is absent in the case of fermentation by yeast.

The production of gas may be considered as the principal characteristic of fermentation proper, and the biological significance of this is the mechanical transportation of the microbes towards the surface of the liquid, where they gain access to oxygen. Hydrogen, the formation of which requires great expenditure of energy, is, on account of its low density, of great importance for this purpose.

A. R. L.

How are Nodule-bearing Leguminosæ enabled to utilise Free Atmospheric Nitrogen? By F. NOBBE and L. HILTNER *Landw. Versuchs-Stat.*, 42, 459—478).—The results of experiments hitherto made on the fixation of free nitrogen seem to indicate that the albumen of the bacteroids, which finally benefits the plant, is produced in a process of life of the bacteria, so that the nodules might be compared with insectivorous plants. But there was no proof that the *Bacillus radicola* could fix nitrogen to any extent, the small gain noticed by Beyerinck (*Abstr.*, 1892, 1019) being quite incomparable with the enormous gains observed in leguminous plants under the influence of the symbiosis. Bacteria are converted into bacteroids at an early stage, but the resorption of the bacteroids does not take place until long after nitrogen assimilation has commenced; moreover, the total nitrogen of the nodules would by no means account for the very large amounts found in the plants.

The results of the authors' experiments now described, when taken together, show that the assimilation of nitrogen is connected with the production of bacteroids. In the first experiments (the summer of 1891), peas were infected with pure cultivations of nodule bacteria. Nodules were formed unusually quickly, but the infected plants were even less vigorous than those which were not infected. The nodules were found to contain immense numbers of unchanged bacteria, but no bacteroids. Early in 1892, a similar experiment gave the usual result, production of nodules and increased growth; and the same result was obtained in a third experiment commenced 12th July. A fourth experiment, however, made at the end of July, gave results similar to those obtained in 1891. Plants which were seeded, and at the same time received 0.35 gram of nitrogen, had normal nodules, and grew well. Other plants, which were not inoculated, but received the same amount of nitrogen as the first, remained free from nodules,

were vigorous, but produced less growth than the manured and seeded plants. Whilst the third series, which were inoculated, but received no combined nitrogen, showed very little development; there were many nodules, some of which were larger than those of the first series, but they contained unchanged bacteria instead of bacteroids. In one pot of this series, four of the plants began early in October to show some vigour, and their nodules were in part normal. It is thus seen that a pure cultivation of *B. radiculicola* may at one time give rise to nitrogen assimilation, and that the same cultivation may suddenly cause plants to fail, although in this case nodules are produced as in the first. The reason of this is the increased vegetative power of the bacteria through cultivation on gelatin. This is shown by the much more rapid growth on gelatin in the summer than early in the year, and by the quicker production of nodules. The influence of the plant, as regards bacteroid formation, was obviously lessened by the increased vigour of the bacteria, but increased under the influence of nitrogenous manure. Nodules containing bacteria only were injurious rather than beneficial to the plant. Unchanged bacteria seem to have nothing to do with nitrogen fixation, which only commences with the production of bacteroids. Under natural conditions, the two factors necessary for the production of abnormal nodules (namely, abnormally vigorous bacteria and soil free from nitrogen) are wanting.

Experiments were next made to ascertain whether the bacteria of all the Leguminosæ belong to one or several varieties. Various plants were grown in soil and in nitrogen-free sand, and infected with pea and with *Robinia* bacteria. *Lupinus luteus* and *angustifolius*, *Acacia Lophanta*, and *Julibrissin* produced nodules only when grown in sand, whilst peas and *Robinia* plants produced nodules both in soil and in sand. In the case of lupins and acacia, the plants are only able to be infected by these bacteria when they have reached the period of hunger. As regards the size of nodules, larger nodules were formed in nitrogen-free sand than in nitrogenous soil. The difference was very marked in the case of *Robinia*. *Robinia* plants were grown without nitrogen, with 10 milligrams of nitrogen, and with 100 milligrams of nitrogen; there was a similar series, but also inoculated. The amount of growth was greatest in the case of the inoculated plant receiving the larger amount of nitrogen; the next in amount of growth was the unseeded plant with 100 milligrams of nitrogen. The growth in the case of the inoculated plant with 10 milligrams of nitrogen was almost as much as the first two, whilst in all the other experiments there was much less growth. A small initial amount of nitrogen is thus practically as effective as a large amount. The large nodules of the seeded plants kept without combined nitrogen contained, besides unchanged bacteria, chiefly bacteria in the first stage of their conversion into bacteroids; they were 0.5 to 0.9 μ thick to 2.5 μ long. The much smaller nodules of the plants manured with nitrogen contained only bacteroids, and these were very large, as much as 9 μ long.

Many leguminous plants, especially *Robinia*, yield a greater final gain of nitrogen when grown in nitrogen-free soil than in soil sup-

plied with combined nitrogen. This is due to the fact that later in the season the conversion of bacteria into bacteroids becomes complete, and the large nodules then give rise to an extraordinarily increased growth, much greater than that induced by the smaller nodules formed under the influence of nitrogenous manure. This probably holds good in the case of yellow lupins (Frank, *Landw. Jahrb.*, 21).

Bacteroids are formed by the division, without separation, of bacteria. In the first stage, the rod divides in the middle; the two poles are coloured, just like the unchanged bacteria, the intermediate space remaining colourless. This process continues, and branches may be formed. It seems probable from their structure that, in the absorption of nitrogen, the bacteroids act like lungs; they offer an enormous surface; or they may be more appropriately compared with gills, if Bouquet's theory of absorption of nitrogen dissolved in water should prove to be correct (*Journ. Agr. Pract. and Bied. Centr.*, 1891, 424). As bearing on this, it may be mentioned that in the author's experiment with *Robinia*, the plant evaporated 12 litres of water and assimilated 600 milligrams of nitrogen, or 50 milligrams per litre. Water at 10° will only absorb about 20 milligrams of nitrogen per litre; but inasmuch as the experiment was in progress for five months, and it is probable that the water near the nodules would become exhausted as regards nitrogen, Bouquet's theory is worth considering. In water cultures, nodules are much less effective than in soil, and this may be due to the slower absorption of nitrogen than in capillary soil.

N. H. M.

Fixation of Nitrogen by Plants. By P. KOSOVITCH (*Izvéstiya Petrovskoi Selskochozyaistvennoi Akademii*, 15, ii, 1—32).—The author has made a series of experiments in order to ascertain whether it is the roots or the leaves of plants which are active in fixing free nitrogen. His method consisted in keeping either the leaves or the roots of the experimental plants (peas) surrounded by an atmosphere of oxygen and hydrogen (the other part being exposed to the air), and, after the lapse of 1—3 months, determining the amount of nitrogen in the plant. The soil was sand freed from nitrogen compounds. He considers that his results go to show that, in papilionaceous plants, the free nitrogen which is fixed is chiefly absorbed through the roots; although he does not deny that some may also be fixed by means of the leaves.

J. W.

Assimilation of Nitrogen by Plants. By E. BRÉAL (*Ann. Agron.*, 19, 274—293).—A number of experiments are detailed by the author from which he draws the following conclusions:—The soils of forests and natural prairies are highly charged with organic matter, forming a medium in which the nitric ferments cannot transform ammonia into nitrate. The vegetation covering these soils is, therefore, obliged to assimilate nitrogen in the form of ammonia.

Grasses, in fact, flourish in nutrient solutions containing nitrogen as ammonia only, quite as well as in those containing the same quantity of nitrogen as nitrate. They even have the power of converting

nitrate into ammonia when a weak solution of nitrate is caused to trickle over them in presence of air and sunlight, and they continue to grow, blossom, and seed, at the expense of the ammonia so produced.

The principal cause of loss of nitrogen by soils, namely, nitrification, being thus very feeble in grass land, such land becomes enriched in organic nitrogen by the operation of the several modes of fixation of atmospheric nitrogen now known to exist.

When grass land is ploughed up, the yield of other crops is by no means proportional to the mass of organic nitrogen accumulated in the soil. No doubt the abundance of insects in pasture soils is one of the causes determining their relative want of fertility; but, in addition to this, the *débris* of the grasses is an absolute hindrance to nitrification; experiment shows that the same soil nitrifies more when unmixed than when mixed with the roots of grasses.

An entire grass crop, ploughed in as manure, augments the nitrification to some extent, but much less than a leguminous crop containing the same quantity of nitrogen.

The hindrance to nitrification is much less when the grass is applied as manure to a rich soil, like garden soil, in which the nitrifying ferments are already abundant, than when it is ploughed in *in situ*. Grass crops ploughed in occasion a loss of nitrogen in the gaseous state. Vegetable matter, ploughed in, acts as a nitrate-reducing ferment; if it is *sterilised* before being mixed with the soil, nitrification is increased. J. M. H. M.

Formation of Citric acid by the Fermentation of Glucose. By C. WEHMER (*Compt. rend.*, 117, 332—333).—Two moulds have the property of fermenting solutions of glucose, juices of fruits, and other liquids containing sugar, with production of a considerable proportion of citric acid. The spores of these moulds are abundant in the air, and are found in widely separated localities. The moulds themselves form at the surface of the liquid in a somewhat thick layer resembling *Penicillium*, but the organs of reproduction are small and the precise description and definition of the species is very difficult. The author calls the two moulds *Citromycetes*, and distinguishes the two species as *pfefferianus* and *glaber*. C. H. B.

Analyses of California Prunes, Apricots, Plums, and Nectarines. By G. E. COLBY (*Exper. Stat. Record*, 4, 918—921; from *Californ. Stat. Bull.*, May, 1893; compare this vol., ii, 140).—The following table gives the percentage amounts of various constituents in the whole fresh fruit and in the juice.

	In fresh fruit.				In juice.	
	Dry matter.	Ash.	Nitrogen.	Sugar.	Sugar.	Acid.
Prunes.....	22·62	0·49	0·162	15·35	20·00	0·40
Plums.....	22·57	0·54	0·181	12·89	17·97	0·48
Apricots.....	14·84	0·49	0·194	11·10	13·31	0·68
Nectarines.....	21·00	0·50	0·117	14·11	17·17	0·62

The composition of the ash of the whole fruit, (1) French prunes and (2) Royal apricots, was found to be as follows :—

	K ₂ O.	Na ₂ O.	CaO.	MgO.	P ₂ O ₅ .	MnO ₂ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
1.	63·83	2·65	4·66	5·47	2·72	0·39	14·08	2·68	3·07	0·34
2.	59·36	10·26	3·17	3·68	1·68	0·37	13·09	3·63	5·23	0·45

As regards amounts of minerals removed from soils by different fruits, grapes come first, then figs, oranges third, and prunes, apricots, and plums fourth. This refers to fruit grown in the United States, which differs from European fruit in the amount of ash constituents.

N. H. M.

Chemical Changes in Tobacco during Fermentation. By S. W. JOHNSON (*Exper. Stat. Record*, 4, 910—911; from *Conn. State Stat. Rep.*, 1892).—Duplicate samples of upper leaves, leaves lower down on the stalks, and best leaves were selected, and in each case one sample was analysed at once; the other fermented before analysis. In fermenting, there was a loss of 9·7, 12·3, and 9·1 per cent. in the upper, lower, and best leaves respectively, chiefly due in the case of the lower leaves to the evaporation of water, but in the case of the upper leaves to loss of dry matter. The best leaves lost about equal amounts of water and dry matter. The loss of nicotine amounted to over one-third in the upper leaves, less than half in the lower leaves, and less than one-sixth in the best leaves. The upper leaves lost over one-seventh of the nitrogen-free extract, and one-fifth of the ether extract. The best leaves lost chiefly nitrogenous matters other than nicotine and nitrogen-free extract, including the "gum" of tobacco.

N. H. M.

Analyses of Tobacco Stalks when cut and after curing. By S. W. JOHNSON (*Exper. Stat. Record*, 4, 911—912; from *Conn. State Stat. Rep.*, 1892).—Three lots of four tobacco plants were selected on 22nd August. No. 1 was cut, whilst still unripe, the same day. Nos. 2 and 3 were cut, when ripe, on the 7th September. 1 and 3 were analysed at once, 2 after being cured until 16th October. The following table gives the total amounts of stalks and the constituents in lbs. per acre.

	Total weight.	Dry matter.	Starch.	Dextrose.	Nicotine.	Nitrogen.
1.	9·437	1·279	147	38·0	6·6	25·5
2.	3·438	1·323	171	8·7	?	41·8
3.	9·750	1·328	189	36·0	8·8	32·2

	P ₂ O ₅ .	K ₂ O.	Na ₂ O.	CaO.	MgO.	$\frac{\text{Fe}_2\text{O}_3}{\text{Al}_2\text{O}_3}$.	SO ₃ .	Cl.
1.	5·5	47·8	1·1	11·9	5·6	1·2	6·8	5·6
2.	7·9	54·7	0·9	14·7	6·9	0·7	7·4	6·8
3.	5·8	50·6	1·1	15·4	6·8	1·3	6·3	6·5

The stalks thus gained in nearly every constituent in the period of growth between 22nd August and 7th September.

N. H. M.

Swedish Fodder Plants. By A. G. KILLGREN and L. F. NILSON (*Exper. Stat. Record*, 4, 971—973; from *Kgl. Landtbruks Akad. Handl.*, 32, 88—106).—The composition of five phanerogamous and

four cryptogamous plants from N. Sweden was determined. The plants are all used more or less as fodder. The plants analysed were (1) *Alchemilla vulgaris*, (2) *Epilobium alpinum*, (3) *Melampyrum pratense*, (4) *Malgedium alpinum*, (5) *Stellaria graminea*, (6) *Equisetum fluviale*, (7) *E. palustre*, (8) *Cetraria nivalis*, (9) *Cladonia rangiferina*. The dry matter had the following percentage composition:—

	Ash.	Crude protein.	Ether extract.	Crude fibre.	Nitrogen- free extract.	Nitrogen.	Digested nitrogen.
1.	8·33	13·19	4·13	14·90	59·36	2·11	1·98
2.	11·35	15·43	3·61	13·49	56·12	2·47	2·29
3.	7·89	12·06	1·67	24·07	54·31	1·93	1·14
4.	16·17	14·43	3·43	20·18	45·79	2·31	1·94
5.	5·94	10·88	2·10	24·65	56·43	1·74	1·39
6.	17·54	10·57	1·57	20·09	50·23	1·69	1·40
7.	17·17	15·84	2·46	14·48	50·05	2·53	2·24
8.	0·86	2·17	3·57	2·65	90·75	0·35	0·19
9.	0·59	1·83	1·87	95·71		0·29	0·17

The small amount of nitrogen in the two lichens (8 and 9) is remarkable considering that they form the sole food of the reindeer for a part of the year. The amount of moss which the reindeer would have to consume daily according to the German feeding standards would decidedly exceed the capacity of the animals. The reindeer-moss (9) is used for cattle, whilst the *Cetraria* is mostly fed to sheep. The lichens are treated with hot water and sometimes mixed with barley or oatmeal, and salt before being fed.

N. H. M.

Experiments with Ammonium Sulphate and Sodium Nitrate for Barley and Oats. By S. RHODIN (*Exper. Stat. Record*, 4, 965—966; from *Kgl. Landtbruks Akad. Hand.*, 30, 142—148 and 32, 78—82).—Experiments hitherto made in England and Germany on the relative value of ammonium salts and nitrate for potatoes and roots showed that the nitric nitrogen is considerably the more effective. With cereals, the results are, however, conflicting. Whilst Lawes and Gilbert found that 100 lbs. of nitric nitrogen increased the yield of barley and wheat by 50 lbs. of grain and 100 lbs. of straw above the yield obtained by the application of the same amount of nitrogen as ammonia, Maercker, experimenting with barley and oats, and Wagner, experimenting with oats, rye, and other crops, found the value of nitrogen in the two forms to be about the same. In the author's experiments, barley and oats were grown in a heavy clay, rich in potash and phosphates, and supplied with sodium nitrate and with ammonium sulphate. The weather was unfavourable during the two years of the experiment. Taking the average yields, it was found that barley was more benefited by the nitrate than by the ammonia, whilst in the case of oats the ammonia was somewhat more effective than the nitrate.

N. H. M.

Manuring Potatoes. By EDLER (*Bied. Centr.*, 1893, 657—659).—Comparison of the effects of potash, nitrogen, and phosphorus

manures on the yield and composition of potatoes showed that phosphates alone had no effect whatever on the increase, but rather caused a decrease when employed in conjunction with nitrogen or potash.

Potash in all cases increased the yield, which was still further added to by the action of nitrogen.

Unmanured potatoes contained most dry matter and starch, the percentage thus obtained being closely approached by that found when potash alone was applied.

The author considers that there is an insufficiency of potash and nitrogen in a soil to permit of a full yield of tubers, consequently there must be some assistance; on the other hand, there is enough of phosphates to produce a normal yield, and no further addition of this manure is necessary.

E. W. P.

Available Phosphoric acid and the Soluble Potash in Cotton Seed Meal. By M. B. HARDIN (*Exper. Stat. Record*, 4, 901; from *S. Carolina Stat. Bull.*, Dec., 1892).—In the original paper, tables are given showing the soluble, insoluble, reverted, and total phosphoric acid, and the total soluble potash, in 13 samples of cotton-seed meal. The average meal (with about 7 per cent. of nitrogen) contains nearly 2.5 per cent. of available phosphoric acid and a little more than 1.5 per cent. of soluble potash, corresponding with over 0.9 and 0.8 per cent. of the total phosphoric acid and potash respectively.

N. H. M.

Analytical Chemistry.

The Oxy-coal-gas Flame for Spectrum Analysis. By O. VOGEL (*Zeit. anorg. Chem.*, 5, 42—62).—The author finds that the characteristic spectra of the elements are more easily obtained in the flame of a burner fed with coal gas and compressed oxygen than in the flame of a bunsen burner. For, whilst minerals must be decomposed and their constituent metals converted into volatile salts in order that the spectra may be produced by a bunsen flame, there is no need for this preliminary treatment when an oxygen-fed flame is employed. The elements may be classified according to the ease with which they yield characteristic spectra; (I) in a bunsen flame; (II) in an oxygen-fed coal gas blow-pipe; (III) in a spark apparatus; and (IV) in an absorption spectrum apparatus.

I. Sodium, potassium (lithium), strontium, calcium, barium.

II. Barium, boron, lithium, indium, thallium, rubidium, caesium, manganese, lead, copper, bismuth (antimony, tin, magnesium).

III. Zinc, cadmium, mercury, silver (magnesium).

IV. Magnesium, aluminium, iron, cobalt, nickel, chromium, uranium, manganese (as permanganic acid).

The most marked advantage gained by the use of the oxygen-fed

flame is in the more refrangible end of the spectrum, where the lines appear much more brightly than with the bunsen flame.

The author finds that lithium is far more widely distributed in nature than is generally supposed. A. G. B.

Quantitative Separation of Iodine, Bromine, and Chlorine: Estimation of Bromine in Mineral Waters and Mother Liquors. By P. JANNASCH and K. ASCHOFF (*Zeit. anorg. Chem.*, 5, 8—12).—The authors depict a convenient apparatus for the separation of bromine from chlorine by the method which they have already described (this vol., ii, 295), and quote some analyses of mineral waters and mother liquors in illustration of the applicability of the method. Hydrocyanic acid may be estimated with accuracy by acidifying the solution under examination with a few drops of sulphuric acid, distilling in a current of steam, and absorbing the acid vapour in a solution of sodium hydroxide, from which the cyanide may be precipitated as silver cyanide. A. G. B.

Reduction of Nitric acid by Ferrous Salts. By C. F. ROBERTS (*Amer. J. Sci.*, 46, 126—136).—The author has made numerous experiments to ascertain why the estimation of nitrates by means of ferrous salts generally gives results which are too low. The apparatus used consists of a small, tubulated retort, upon the neck of which is fitted a small condenser to prevent loss of liquid during the distillation. Into the tubulure of this retort is fixed tightly, by a carefully ground joint, a tube drawn out so as to dip below the surface of the liquid, and fitted with carefully ground stop-cocks, and so branched above as to make it possible to transmit carbonic anhydride through the apparatus, or to admit any liquid without air entering. The condenser is joined to a Will and Varrentrap nitrogen bulb, used as a trap, and this connected by thick vacuum tubing with a Hempel gas burette filled with aqueous soda. About 0.1 gram of the nitrate is introduced into the retort, preferably in the dry state. Carbonic anhydride, generated from marble and hydrochloric acid containing a little cuprous chloride, is passed until it is practically all absorbed by aqueous soda, and 40 c.c. of a solution of ferrous chloride is then admitted through the funnel tube after shutting off the gas and lowering the levelling tube of the burette. The liquid is then boiled until all the nitric oxide has been expelled, and its complete removal is secured by a further passage of carbonic anhydride. The volume of the gas in the burette is then noted with the usual precautions. To see how much of it consists of nitric oxide, the author prefers to absorb it by means of potassium permanganate. In some experiments, a solution of potassium iodide was introduced into the nitrogen bulbs, to reduce any higher oxides of nitrogen. As the result of many experiments, the author finally draws the following conclusions:—1. The best results are obtained when the gas is passed through solution of potassium iodide. 2. If small amounts of air have got into the apparatus, they will not affect the total volume of gas if potassium iodide be not used; but if this is used, the error will be still greatly reduced by the solubility of nitric oxide in aqueous soda. 3. On

account of this slight solubility, the gas should not be left too long in contact with the alkali. 4. If the hydrochloric acid used is very dilute, the reaction proceeds very slowly, but the result is not affected. 5. If the nitrate and the ferrous chloride are mixed whilst hot, higher oxides of nitrogen are formed, but they are again reduced by the potassium iodide. 6. If potassium iodide is used, there is no need for a large excess of iron.

L. DE K.

Estimation of Chlorates and Nitrates, and of Nitrites and Nitrates in one Operation. By C. F. ROBERTS (*Amer. J. Sci.*, 46, 231—235).—The apparatus used is the same as that required for the gas-volumetric estimation of nitric acid by means of an iron salt (see preceding abstract). The mixture, of, say, potassium chlorate and nitrate, is boiled with hydrochloric acid containing manganous chloride. Chlorine is liberated from the chlorate, but also to a certain extent from the nitrate; but the amount of the latter may be accurately determined from the volume of nitric oxide given off. By passing the chlorine through a solution of potassium iodide, estimating the liberated iodine with thiosulphate, and, allowing for the amount of chlorine generated by the nitrate, the analysis may be very accurately carried out. Of course everything depends on the correct measurement of the nitric oxide.

By the action of manganous chloride on a hydrochloric acid solution of a nitrate or nitrite, both chlorine and nitric oxide are given off and may be readily estimated. If the total weight of nitrate and nitrite is known, the proportion of each may be found by indirect analysis. The author thinks this process well suited, at all events, for the assay of commercial nitrites.

L. DE K.

Rapid Estimation of Phosphorus in Iron and Steel. By W. MACFARLANE and A. WILSON (*Chem. Centr.*, 1893, ii, 145—146; from *Iron and Coal Trade Rev.*, 1893, 330).—The authors propose a standard process and also a rapid method:—1. *Standard Process.*—2 grams of the sample is dissolved in a 110 mm. wide beaker, in 15 c.c. of hydrochloric acid (sp. gr. 1.16) and 15 c.c. of nitric acid (sp. gr. 1.42). The solution is evaporated to dryness, and the beaker is put for 10 minutes on a hot plate. After cooling, the residue is dissolved in 20 c.c. of hydrochloric acid, the solution is boiled down to half, diluted with 20 c.c. of hot water, and filtered into a 700-c.c. beaker. After neutralising with ammonia, the iron is reduced by means of ammonium hydrogen sulphite, the excess of sulphurous acid is boiled off, and a slight excess of ferric chloride is added. The phosphoric acid is now precipitated as ferric phosphate by the cautious addition of ammonium carbonate; the precipitate is washed twice with hot water on a filter, and redissolved in dilute hydrochloric acid. The solution is supersaturated with ammonia, the precipitate redissolved in nitric acid, and the liquid, after heating to 85°, mixed with 200 c.c. of molybdate mixture. The precipitate is washed with dilute nitric acid (1—20), and dissolved in dilute ammonia (1—8). The solution is nearly neutralised with ammonia, magnesium mixture is added, and

then again one-sixth of the bulk of ammonia; the precipitate formed is treated as usual.

2. *The Rapid Method.*—The sample is dissolved as before and made up at once to 250 c.c.; 20.28 c.c. is put into an Erlenmeyer flask and mixed first with 2 c.c. of ammonia and then with a slight excess of hydrochloric acid; 17 c.c. of ammonium nitrate solution is added, the liquid is heated to 85°, and, after the addition of 20 c.c. of molybdate solution, it is well shaken for one minute. The precipitate is filtered off, washed three times with dilute nitric acid (1—50), rinsed into a tared dish, dried, and weighed. The weight multiplied by 10 represents the amount of phosphorus in the sample. This process is particularly suitable for the analysis of pig iron. When dealing with cast-iron, 2 grams is dissolved in 20 c.c. of nitric acid and 7 c.c. of water, the solution is evaporated to dryness and heated for five minutes on a hot plate. The residue is then treated with 15 c.c. of hydrochloric acid, evaporated to a syrupy consistence, rinsed into an Erlenmeyer flask, mixed with 15 c.c. of ammonium nitrate solution, and heated to 85°; finally, the phosphoric acid is precipitated by adding 15 c.c. of molybdate solution.

To estimate phosphoric anhydride in slags, 0.5 gram of the sample is dissolved in 8 c.c. of hydrochloric acid. After adding 12 c.c. of water, the liquid is evaporated down to 10 c.c., filtered into a 250-c.c. flask, and made up to the mark. 25 c.c. of the solution is then treated with 18 c.c. of ammonium nitrate solution, and 20 c.c. of molybdate solution, as before.

L. DE K.

Volumetric Estimation of Phosphates. By C. WAVELET (*Chem. Centr.*, 1893, ii, 145; from *Schweiz. Woch. Pharm.*, 21, 173—174).—The author recommends the volumetric lead process originally suggested by Mohr and Schwarz. The following solutions are required, 1. A standard solution containing 10.085 grams of (dry) sodium hydrogen phosphate per litre. 2. A solution of 50 grams of sodium acetate per litre. 3. A solution of 40 grams of lead nitrate per litre. 4. A 5 per cent. solution of potassium iodide, contained in a bottle made of yellow glass. 70 c.c. of the phosphate solution is mixed with 5 c.c. of the sodium acetate, and the lead is then added from the burette until precipitation ceases, the potassium iodide serving as indicator. A blank experiment, without phosphate, should also be made, and the result corrected thereby.

For the assay of commercial phosphates, 5 grams of the sample is dissolved in nitric acid and diluted to 250 c.c. 50 c.c. is then titrated with lead solution.

L. DE K.

Volumetric Estimation of Pyrophosphoric acid and Alkali Pyrophosphates. By G. FAVREL (*Bull. Soc. Chim.*, [3], 9, 446—448).—Pyrophosphoric acid acts as a monobasic acid in presence of cochineal as indicator, and as a bibasic acid in presence of soluble blue (Poirrier's C4B) at the ordinary temperature.

Alkaline pyrophosphates free from alkali hydroxides or carbonates can be directly titrated by standard acid in presence of cochineal. If alkali hydroxides be present, separate portions are titrated using

cochineal, and soluble blue respectively; the difference gives the amount of pyrophosphoric acid present. If alkali carbonates are present, the total alkali is titrated with cochineal, then, to a second portion of the liquid, the same amount of standard acid is added, and the mixture titrated with standard soda using soluble blue as indicator; the amount of soda solution used gives the amount of pyrophosphoric acid present.

In presence of phenolphthaleïn, pyrophosphoric acid requires for neutralisation 2 mols. of calcium or strontium hydroxide, or $1\frac{1}{2}$ mols. of barium hydroxide, W. T.

Volumetric Estimation of Alkalis in Alkali Arsenites. By G. FAVREL (*Bull. Soc. Chim.*, [3], 9, 448—449).—Arsenious acid is indifferent to cochineal, but exerts some acid reaction on phenolphthaleïn and more on soluble blue (Poirrier's C4B).

In presence of cochineal, alkalis combined with arsenious acid can be directly titrated with standard acid. Results given show a substantial agreement between the amounts of potash determined by titration and by the platinochloride methods. W. T.

Toxicological Examination for Metals. By M. GARNIER (*J. Pharm.*, [5], 28, 193—195).—The organic matter is destroyed by oxidation with potassium chlorate, and hydrochloric acid prepared from fused purified sodium chloride and pure sulphuric acid. The metals are precipitated by sulphuretted hydrogen, slowly evolved by a continuous apparatus, and washed by passage through potash solution and distilled water in succession. W. T.

Direct Estimation of Potassium and Sodium by means of Tartaric acid. By A. BAYER (*Chem. Zeit.*, 17, 686—687).—The author adds to the solution a quantity of sodium carbonate sufficient to combine with any sulphuric, phosphoric, or hydrochloric acid present, and, after adding some acetic acid, tartaric acid is added in excess; the liquid is warmed for some time, mixed with one-third of its bulk of alcohol, and allowed to settle for two hours. The solution is then passed through a filter, and the precipitate of potassium hydrogen tartrate is first washed slightly with 25 per cent. alcohol and then thoroughly with 50 per cent. alcohol. It is now dissolved in boiling water, and titrated with decinormal soda, using phenolphthaleïn as indicator. The test analyses prove the method to be quite as trustworthy as the platinic chloride process.

Sodium may be estimated directly, in presence of potassium, by boiling with ammonium hydrogen tartrate and a little acetic acid. When cold, the liquid is mixed with one-third of its bulk of absolute alcohol, and, after some time, made up with 25 per cent. alcohol to a definite bulk: for instance, 250 c.c. An aliquot part, say 200 c.c., is now filtered and evaporated, with the addition of a little nitric acid, and the residue is gently ignited and then extracted with water. The sodium, after the usual treatment with barium chloride to decompose sulphates, &c., is finally weighed as chloride. As, however, potassium hydrogen tartrate is not quite insoluble in 25 per cent. alcohol, the amount of sodium chloride found will be somewhat

too high, but this may be remedied by allowing 0.0348 gram of potassium chloride for every 200 c.c. of alcoholic filtrate.

L. DE K.

Volumetric Estimation of Lead. By ALEXANDER (*Chem. Centr.*, 1893, ii, 293—294; from *Engin. and Min. Journ.*, 55).—Ammonium molybdate causes, in a lead solution, a precipitate of lead molybdate insoluble in acetic acid. 0.5—1 gram of the sample of lead is dissolved in a mixture of sulphuric and nitric acids, and evaporated until sulphuric fumes begin to escape. When cold, the liquid is diluted with cold water, then heated for some time, and filtered; the precipitate is washed with dilute sulphuric acid, dissolved in ammonium acetate, acidified with acetic acid, and diluted with boiling water to 250 c.c. The molybdate solution is then added from a burette until all the lead is precipitated, which may be ascertained by adding a drop of the supernatant liquid to a drop of tannic acid solution (1—300), which will give a yellow colour should the least excess of molybdenum be present. The molybdate solution is prepared by dissolving 9 grams of ammonium molybdate in a litre of water to which a few drops of ammonia have been added. The analysis takes about an hour.

L. DE K.

Detection and Estimation of Lead in Tartaric and Citric acids. By R. WARINGTON (*J. Soc. Chem. Ind.*, 12, 97—104, 222—225).—The author first calls attention to the occasional presence of visible fragments of metallic lead, probably fine scrapings of metallic lead left by plumbers when mending the leaden vessels. Both tartaric and citric acid crystals have occasionally attached to their base, where they have been in contact with the leaden vessel, patches of an opaque, whitish substance, which is evidently a portion of the corroded surface of the lead removed by the crystal. This substance does not always entirely dissolve in water, but it does so very rapidly when excess of ammonia is added. The author has, however, generally found the lead to pass into the aqueous solution. After describing the various pharmacopœia tests, British and foreign, for the detection of lead in tartaric and citric acids, the author finally recommends the following process. 40 grams of the sample is dissolved in a little water, and pure, strong ammonia is added in slight excess; the liquid is then cooled and diluted to 120 c.c. As a preliminary experiment, 10 c.c. is taken, diluted to 50 c.c., and mixed in a Nessler tube with 1 drop of solution of ammonium sulphide; the colour developed indicates what volume of solution should be taken for the determination, and this may range from 5 to 50 c.c. The tint has now to be matched with the pure solutions. A volume of pure ammoniacal tartrate or citrate solution identical with that taken of the acid under examination is mixed with a measured quantity of a slightly acid lead nitrate solution, containing 0.1 gram of metallic lead per litre. A drop of ammonium sulphide is then added, and, should the coloration be too light or too dark, the experiment must be repeated until a perfect match is obtained, just as in Nesslerising water. The amount of iron present in commercial tartaric or citric acid is, as a rule, too small

with the test. A considerable amount of iron will be at once indicated by an abnormal blackish colour. The presence of copper will betray itself by a bluish coloration on adding the ammonia. Both iron and copper may, however, be rendered harmless by the addition of a drop of a solution of potassium cyanide before adding the ammonium sulphide.

As it is well-nigh impossible for a manufacturer to produce an acid absolutely free from lead, the author proposes the following standard of purity. The proportion of lead in either tartaric or citric acid should not exceed 5 parts per million, when tested by the method described.

L. DE K.

Detection of Lead in Urine. By L. K. FRANKEL (*Chem. News*, 68, 5).—The author states that it is possible to detect 1 part of lead, dissolved in nitric acid, in 1,000,000 parts of water, by means of the deposit of peroxide formed on a platinum electrode when the solution is electrolysed. The presence of urine prevents this deposition of peroxide from the solution of the nitrate, and, instead, a deposit of lead is obtained on the negative electrode; but no deposit at all is obtained when urine containing lead that has passed through the animal system is electrolysed, even when the current has passed sufficiently long to oxidise the seum and mucus which at first collects on the surface. Therefore, to test for lead in urine, the author oxidises the organic matter with potassium chlorate and hydrochloric acid, and, subsequently, treats the solution with hydrogen sulphide.

D. A. L.

Separation of Iron, Aluminium, Manganese, Zinc, and Calcium. By B. KOSMANN (*Chem. Centr.*, 1893, ii, 155; from *Stahl. u. Eisen*, 13, 431).—The author uses the process recommended by Riggs (compare Abstr., 1892, 916), but instead of adding ammonium acetate, solid ammonium carbonate is first added, and then a proper amount of acetic acid.

L. DE K.

Separation of Arsenic and Antimony. By L. GARNIER (*J. Pharm.*, [5], 28, 97—99).—The author has critically examined a method given by Dragendorff for the separation of arsenic and antimony in toxicological researches.

The sulphides of these metals cannot be even approximately separated by the difference of their solubility in dilute ammonia, hence Dragendorff's method based on this difference cannot be employed in practice.

Ritter's method of treating the mixed mirror obtained by Marsh's method, in which finally the arsenic is precipitated as ammonium magnesium arsenate, is the best.

W. T.

Stability of Standard Solutions of Tartar Emetic. By H. GRUENER (*Amer. J. Sci.*, 46, 206—208).—The author has found that solutions of tartar emetic, containing 16 grams of the salt per litre, form a deposit after several months, and that this sediment, chiefly a fungoid growth, contains a large proportion of antimony. But as the total quantity of deposit is but very slight, the strength of the solution is not greatly affected.

The fungoid growth may, however, be practically prevented by adding 20—30 grams of tartaric acid and also 1 c.c. of strong hydrochloric acid per litre.

L. DE K.

Estimation of Nitrogen in Soils. By F. W. DAFERT (*Exper. Stat. Record*, 4, 961; from *Rel. Inst. Agron. São Paulo, Brazil*, 1892).—The author recommends steam distillation for expelling the ammonia from the alkaline solution obtained in the Kjeldahl process. The danger of bumping is overcome, and the time required for distillation reduced to 6—10 minutes. When the soil contains much insoluble matter, the solutions should be filtered before distilling.

N. H. M.

Estimation of Sugars by means of Fehling's Solution. By E. NIHOUL (*Chem. Zeit.*, 17, 500).—The cuprous oxide is most conveniently collected on a tared filter and weighed as such. The author finds that filters after being immersed in alkaline copper solutions may be completely freed from copper by washing with water. Prolonged drying at 70—100° does not in the least increase the weight of the suboxide, but it is always contaminated with organic matter, and in accurate analyses an allowance of 0.3—0.4 per cent. should therefore be made.

Cuprous oxide may be readily converted into cupric oxide by treatment with nitric acid and ignition. With care, no loss will occur, Soxhlet's view that it volatilises to a certain extent as oxynitrate being erroneous.

L. DE K.

Estimation of Isomaltose in Worts. By A. BAU (*Chem. Zeit.*, 17, 499).—The author bases his process on the fact that isomaltose is not fermented by ordinary yeast, but suffers fermentation by *Saazer* yeast.

A quantity of wort is allowed to ferment with common yeast, and any invertible sugar left is then estimated in the ordinary way. A similar quantity of the wort is at the same time fermented with the *Saazer* yeast, and any sugar is then also estimated. The difference between the two determinations represents the amount of isomaltose. It must be remembered that 100 parts of isomaltose, on inversion, yield 105.3 parts of dextrose.

The presence of isomaltose may be proved qualitatively by the reaction with phenolhydrazol acetate.

L. DE K.

Estimation of Glycogen. By E. PFLÜGER (*Pflüger's Archiv*, 53, 491—492).—R. Külz (*Zeit. Biol.*, 22, 192) points out that in the separation of proteid from glycogen by Brücke's reagent one often obtains a persistently cloudy filtrate. This difficulty can be met by reprecipitating by alcohol, then dissolving the precipitate in 2 per cent. potassium hydroxide, neutralising with hydrochloric acid, and again adding Brücke's reagent.

W. D. H.

Estimation of Fat in Milk. By WEISS (*Chem. Centr.*, 1893, ii, 159; from *Pharm. Zeit.*, 38, 258).—The author's process (this vol.,

ii, 396), extraction of the fat by means of light petroleum, having been adversely criticised by Strassmann, attention is again called to the following important points.

1. The light petroleum containing the fat should be poured off after three hours when testing milk poor in cream; when the sample is very creamy, 12 hours should elapse. 2. A quarter of an hour before pouring off, the mixture should be once more thoroughly shaken. 3. The residual fat must be dried to constant weight, and as it obstinately retains petroleum, the temperature should be raised to 110° . 4. When reading off the volume of the petroleum layer, the temperature should be noted, and an aliquot part should be pipetted off at the same temperature. To prevent errors arising from expansion or contraction, the author recommends weighing instead of measuring the light petroleum.

L. DE K.

Analysis of Butter. By E. LAVES (*Arch. Pharm.*, **231**, 356—366).—The author has examined the method of König and Hart (*Abstr.*, 1891, 1301), and finds that it does not give more concordant results than the Reichert-Meissl-Wollny process, but it is more accurate than the other methods. A slight modification was introduced. Instead of boiling in the reflux apparatus for $3-3\frac{1}{2}$ hours, the boiling is continued for $\frac{3}{4}$ hour only, using 60 c.c. of alcohol, and 7.0 grams of baryta; 50 c.c. of water (previously heated to $70-80^{\circ}$) is added, the mixture boiled for $\frac{1}{4}$ hour, diluted with 190 c.c. of hot water, and again raised to boiling. After being partially cooled, it is treated for five minutes with a stream of carbonic anhydride, filtered, again treated with carbonic anhydride, and boiled vigorously for five minutes in a reflux apparatus; it is then quickly cooled to 20° , filtered, and the barium in the filtrate determined by titration with N/10 sulphuric acid, using tropæolin OO as indicator; or, more accurately, by titrating with a solution of potassium dichromate (of strength equivalent to N/10 barium chloride) in the presence of alcohol and acetic acid, until a drop of the solution gives a blue colour to paper impregnated with tetramethylparaphenylenediamine. Or the barium may be precipitated as sulphate and estimated gravimetrically.

C. F. B.

Sulphuric acid Hydrolysis of Butter-fat. By S. RIDEAL (*Analyst*, **18**, 165—168).—The idea of substituting sulphuric acid for alcoholic potash in effecting the saponification of butter-fat has been worked out by Kreis, and also by Pinette and others. The author has tried the process with very satisfactory results, the figures obtained being practically the same as those got by the Reichert-Meissl process.

10 c.c. of sulphuric acid of sp. gr. 1.836 is added to 2.5 grams of melted butter-fat. After a few minutes, 100 c.c. of water is added, and the mixture shaken, which causes the fatty acids to separate in white flakes. Solution of potassium permanganate is now added until the liquid acquires a pink colour, which is permanent for a few seconds. The mixture is then distilled with the usual precautions

until 80 c.c. has passed over, and the distillate is titrated with decinormal soda, L. DE K.

Discrimination of Butter from Margarin. By F. GANTTER (*Zeit. anal. Chem.*, **32**, 411—413).—The method described by the author for the estimation of cotton-seed oil in lard (this vol., ii, 440) serves equally well for the detection of margarin in butter. The iodine number for genuine butter varies from 13 to 16 when determined by the author's process (this vol., ii, 309); that of margarin is variable according to the kind of fat or oil employed in its manufacture, but always much higher, so that an iodine absorption exceeding 16 per cent. would indicate adulteration. Mixtures of butter with earth-nut oil, whose absorption is 49—51, were found to have iodine numbers corresponding with the proportions of the two fats. Genuine butter gives only a straw-yellow to reddish-yellow colour with strong sulphuric acid; most of the oils used in making margarin give a dark brown colour. M. J. S.

Detection of Heated Cotton-seed Oil in Lard. By W. G. CROOK (*Analyst*, **18**, 221).—The author recommends the following process which will detect 1 per cent. of heated cotton-seed oil in lard:—A small disc of white filter-paper, purified with hydrochloric acid and well washed, is just moistened with a 12 per cent. solution of silver nitrate and placed in the concave part of a watch-glass, which is then inverted over a cup-shaped porcelain capsule of about $\frac{1}{2}$ oz. capacity, containing about 0.75 gram of the suspected sample. The capsule is now placed in an oil bath, which is then slowly heated until the temperature just reaches 115.5°. A more or less marked discoloration on the disc proves the presence of cotton-seed oil.

L. DE K.

Rapid Saponification of Oils. By A. SMETHAM (*Analyst*, **18**, 193—196).—When mixtures of fatty and mineral oils are treated with alcoholic potash, some difficulty is experienced in completely saponifying the glycerides, as they are obstinately retained by the mineral oil which is generally but slightly soluble in the alcoholic liquid.

The author has greatly improved the process by adding to the usual mixture of oil and alcoholic potash about 20 c.c. of ether. The saponification is conducted in flasks of 6 oz. capacity, fitted with glass tubes 3 feet long, and is generally complete within 15 minutes.

L. DE K.

Analysis of Oils. By W. FAHRION (*Chem. Zeit.*, **17**, 434—436).—The author some time ago attributed the gradual fall in the iodine number of oils to polymerisation setting in, and has since confirmed his views. When such polymerised oils are saponified, the acids seem temporarily to revert to their original condition, and the author therefore estimates the iodine number as follows. 0.15—0.25 of the oil is completely saponified with alcoholic soda, phenolphthaleïn is added, and the liquid exactly neutralised with N/2 hydrochloric acid. The iodine absorption is then estimated by means of Hübl's solution,

chloroform being, however, omitted. It appears that even apparently fresh oils are already to a certain extent polymerised, as the iodine absorptions by the author's method give results greatly in excess of the ordinary method. A sample of cotton oil, for instance, gave 104.8 per cent. by the old method, and 150 per cent. by the modified process. L. DE K.

New Method of Fat Analysis. By W. FAHRION (*Chem. Zeit.*, 17, 610).—The author has modified Hazura's permanganate process, and operates as follows. 10 grams of the fat is saponified with 10 grams of sodium hydroxide dissolved in dilute alcohol. After the alcohol has been expelled, the soap is dissolved in 1 litre of water, and heated to boiling. According to the iodine number of the fat, 10–25 grams of potassium permanganate, dissolved in 200–500 c.c. of water, is slowly added, and the boiling is continued for some time. After filtering, the solution is acidified with hydrochloric acid, and, when quite cold, the fatty mass is collected on a cloth, well pressed, and then treated with light petroleum. The solid, also the unoxidised, portions of the fat pass into solution, whilst the oxidation products are left behind, and may be examined afterwards. In special cases, the process may be still further simplified. To test, for instance, for linoleic acid in a non-drying oil, 10 grams of the sample is, as before, oxidised with 10 grams of permanganate. The fatty matter separated by hydrochloric acid is not, however, extracted with light petroleum, but boiled with about 1 litre of water. The liquid is filtered whilst boiling hot, the filtrate is rendered alkaline, concentrated to 100–150 c.c., and, while still warm, introduced into a separating funnel. After adding a slight excess of hydrochloric acid and cooling, the liquid is agitated with ether. If the fat contains oleic acid only, a clear solution is obtained; but should linoleic acid be present, a white, flocculent precipitate of tetrahydroxystearic acid will be noticed. The author has proved the presence of linoleic acid in lard by this process. L. DE K.

Detection and Estimation of Neutral Fats in Mineral Oil. By J. KLIMONT (*Chem. Zeit.*, 17, 543).—The author recommends the following process for the detection and estimation of small quantities of neutral fats in mineral oils. 15 grams of the sample is saponified with 100 c.c. of a 10 per cent. alcoholic solution of potassium hydroxide in a 400 c.c. flask attached to a reflux condenser. After heating for one or two hours, the contents are cooled, mixed with an equal bulk of water, and filtered through a wet filter. The filtrate is then exactly neutralised with hydrochloric acid, and agitated in a separating funnel with light petroleum. The watery layer will, if fat be present, contain potash soap, and consequently give a flocculent precipitate on the addition of calcium chloride.

The same process is suitable for a quantitative estimation of the fat. The aqueous layer is concentrated to about 100 c.c., and precipitated with calcium chloride solution. The precipitate is collected on a weighed filter, well washed, dried at 110°, and weighed. The whole is then burnt to constant weight, and the residual calcium

oxide deducted from the total weight. The fatty anhydride is then calculated to neutral fat. When the amount of fat exceeds 5 per cent., the process is no longer trustworthy. L. DE K.

Analysis of Aniline Oil. By H. REINHARDT (*Chem. Zeit.*, 17, 413—414).—The author's process is based on the facts (1) that aniline, when treated with nascent bromine, yields a tribromo-derivative, whilst ortho- and para-toluidine give dibromo-compounds; (2) that when oxalic acid is added to a hydrochloric acid solution of the three amines, the paratoluidine is precipitated first, the aniline afterwards, and the orthotoluidine not at all. To estimate aniline, or the joint toluidines, or a mixture of the two, the author uses a solution prepared by dissolving 480 grams of bromine and 336 of pure potassium hydroxide in a litre of water, which solution must be well boiled to destroy any hypobromite, and finally diluted to 9 litres. The solution is best standardised by means of pure aniline and toluidine. To carry out an analysis of a commercial sample, about 1.5—2 grams is dissolved in 100 c.c. of hydrobromic acid (sp. gr. 1.45) and 1000 c.c. of water, and the bromine solution is then run in from a burette until a drop of the liquid gives a bluish spot on potassium iodide-starch paper. The proportion of aniline and joint toluidines is now indirectly calculated from the amount of bromine absorbed.

Or 100 grams of the sample is mixed with 106 grams of hydrochloric acid, and then with a calculated slight excess of oxalic acid dissolved in 10 times its weight of water. After 48 hours, the precipitated oxalate is collected, and slightly washed. It is then decomposed by means of aqueous potash, and the liberated oil (paratoluidine and some aniline) is collected and weighed. Any aniline is then estimated by the bromine process. The test analyses are very satisfactory. L. DE K.

Assay of Alkylanilines. By W. VAUBEL (*Chem. Zeit.*, 17, 465—466).—The author recommends the following process. 25 grams of the sample is mixed with 50 c.c. of xylene, and when the temperature has become constant, 25 c.c. of acetic anhydride is added, and the rise in temperature is noticed. A check experiment is now made with 25 c.c. of a mixture of diethylaniline and aniline, containing as much of the latter as the sample shows when analysed by Reverdin and De la Harpe's process. The difference in the two rises in temperature is put down to the presence of monethylaniline, and its proportion is then found by referring to the author's tables.

L. DE K.

Estimation of Hydrazine in Hydrazine Salts. By J. PETERSEN (*Zeit. anorg. Chem.*, 5, 1—7).—The oxidation of hydrazine by Fehling's solution results in the elimination of the total nitrogen in the free state. This fact may be applied to the estimation of hydrazine as follows. An excess of Fehling's solution is diluted to about 60 c.c. and boiled in a flask, provided with a two-holed cork which carries a delivery tube and a glass rod, until all the air has been expelled. The weighed portion of the hydrazine salt is con-

tained in a small tube, which is closed at one end and has its open end thrust into the bottom of that hole in the cork which carries the glass rod; when the air has been expelled from the flask the glass rod is pushed down, and the small tube is thus thrust into the flask. The nitrogen is rapidly evolved and is collected in a measuring tube, boiling being continued until the expulsion of the gas is complete. A correction of $\frac{1}{10}$ c.c. is made for the air retained in the weighing tube.

When hydrazine is oxidised by potassium permanganate in the presence of a 6—12 per cent. solution of sulphuric acid, the reaction which occurs may be represented by the equation $17\text{N}_2\text{H}_4 + 13\text{O} = 13\text{H}_2\text{O} + 14\text{NH}_3 + 10\text{N}_2$. For direct titration, the solution containing the hydrazine must be at a temperature of 60—70°, and the end of the reaction must be taken as that point at which the pink colour, which is some time in completely fading, becomes darker on the addition of more permanganate. For estimation of the nitrogen evolved, the apparatus described above will serve; the hydrogen salt, together with the sulphuric acid, is placed in the flask, and the solid permanganate in the small tube. A trace of oxygen is evolved by the rapid ebullition of the permanganate with the sulphuric acid, so that the gases are collected in a Bunte's burette and this oxygen absorbed before reading the volume of the nitrogen. The estimation of the ammonia is effected by distillation with alkali in the usual manner.

A. G. B.

Detection of Alkaloids, "Saccharin," and Salicylic acid. By LINDEMAN and MOTTEU (*Bull. Soc. Chim.*, [3], 9, 441—446).—The authors have applied the principle of partition of a dissolved substance between two non-miscible solvents to the examination of organic substances and liquids for alkaloids, "saccharin," and salicylic acid.

A solvent having, in comparison with water, a high coefficient of partition is employed. The liquids are carefully placed in contact without mixing; if the aqueous solution be turbid, it is separated from the other solvent by a parchment partition to avoid the introduction of solid particles into the new medium. If the liquid layers are arranged so as not to be thicker than 1 cm., the partition is complete in 24 hours, and the new solvent can be evaporated off and its residue examined.

The examination of beer, milk, coffee, foods, and the body of a poisoned dog has been carried out, known small quantities of strychnine being introduced, and chloroform employed for extraction. Similarly morphine has been determined in beer and urine by chloroform and by amyl alcohol, quinine in beer by chloroform, "saccharin" (benzoic sulphinide) in beer by ether, and salicylic acid in wine and beer by benzene.

W. T.

Volumetric Estimation of the Alkaloids and of some Metals. By D. VITALI (*L'Orosi*, 16, 181—186).—The metals copper, mercury, cadmium, silver, gold, platinum, antimony, and tin, which are completely precipitated from neutral solutions by hydrogen sulphide,

and whose sulphides are insoluble in dilute acids, may be determined in the following manner. The metallic salt (0.5—1.0 gram) is dissolved in distilled water (25—30 c.c.), the solution freed from air by prolonged boiling and precipitated with hydrogen sulphide, care being taken to avoid any contact with the air. The solution is then filtered, the precipitate washed with boiled water, and the filtrate made up to a known volume. On titrating the solution with standard alkali, the amount of acid originally combined with the metal is found, and hence the percentage of the metal itself may be deduced.

Solutions of the hydrochlorides or sulphates of the alkaloids may be precipitated with silver or lead nitrate respectively, and the metal estimated in the precipitate by conversion into sulphide as described above. A simple calculation then gives the proportion of acid in the alkaloidal salt, and consequently the quantity of the alkaloid itself. Both the above methods give good results. W. J. P.

Titration of Morphine. By CANNEPIN and VAN ELJK (*Bull. Soc. Chim.*, [3], 9, 437—441).—The chief sources of error in Portes and Langlois' method have been obviated by following the process detailed below. The original method gave the highest and most concordant results of any of the ordinary processes. The most important sources of loss are—(1) morphine remaining in solution on precipitation, (2) morphine dissolved in the wash water, (3) morphine not extracted from the opium sample by the process.

By the use of lime (3) is rendered very small, and (2) and (1) are largely avoided by using the solutions of morphine indicated below.

10 grams of opium and 4 grams of slaked lime are gradually intimately mixed with 100 c.c. of a solution of 0.805 gram morphine hydrochloride per litre, digested for half an hour, and filtered. 20 c.c. of the filtrate is evaporated at 100°, and the residue weighed. 50 grams (*plus* the weight of solid residue from half the opium, in all about 52 grams) of the filtrate is weighed out, and shaken up with 10 c.c. of ether until saturated; 0.5 gram of ammonium chloride is added, the whole allowed to remain two hours, and then filtered; the precipitated morphine is thoroughly washed with a saturated solution of morphine (0.42 gram crystallised morphine per litre) and dried at 98°. The precipitate may be examined polarimetrically in dilute acetic acid solution, or titrated, using cochineal as indicator. W. T.

Coniine and Nicotine. By G. HEUT (*Arch. Pharm.*, 231, 376—378).—These may be distinguished by adding phenolphthaleïn and chloroform to their aqueous solution and shaking vigorously; in the case of nicotine, the colour then disappears at once; with coniine, it is permanent.

To estimate coniine and nicotine in the presence of each other, dissolve in a small quantity of water, with addition of alcohol; to 50 c.c. of the solution, add 5 drops of chloroform and 1 drop of strong solution of phenolphthaleïn, and titrate with N/10 sulphuric acid until,

on shaking vigorously, the colour disappears ; this gives the conine. To determine the nicotine, now add litmus, and continue the titration with acid. (The colour reaction with litmus is not affected by chloroform.)

C. F. B.

Rapid Estimation of Caffeine in Tea and Coffee. By GUILLOT (*Chem. Centr.*, 1893, i, 865; from *Apoth. Zeit.*, 8, 132).—5 grams of finely-powdered tea is boiled for 20 minutes with 100 c.c. of water, water being added occasionally during the boiling, to restore the loss caused by evaporation. 5 grams of lime is then added, and, after the boiling has been continued for another 15 minutes, the mixture is filtered through a small wet cloth, and the insoluble matter again boiled with 50 c.c. of water, this operation being once more repeated. The united filtrates are now put into a 500 c.c. stoppered separatory funnel, and agitated three times in succession with 60 c.c. of chloroform. When clear, the chloroform is drawn off, filtered through cotton-wool, and evaporated in a tared dish.

The residual caffeine is fairly pure. When applying the process to coffee, this must be coarsely ground, dried, and reduced to a fine powder. It is then boiled with water first for half an hour, then again twice for a quarter of an hour, and finally treated like the tea decoction.

L. DE K.

Separation of Theobromine and Caffeine. By H. BRUNNER and H. LEINS (*Chem. Centr.*, 1892, i, 802; from *Schweiz. Woch. Pharm.*, 31, 85—87).—Süss extracts the raw material with light petroleum to remove caffeine and fatty matter, and then with chloroform to dissolve the theobromine. The authors found, however, that the alkaloïd obtained in this way is not pure, but reduces an ammoniacal solution of silver nitrate, whilst the pure substance yields a white compound of the formula $C_7H_7AgN_4O_2$.

When pure, theobromine may be separated from caffeine by means of silver nitrate. About 0.2 or 0.5 gram of the mixed alkaloids is dissolved in 200 c.c. of water, mixed with 5 c.c. of ammonia, and boiled with 0.6 gram of silver nitrate until the ammonia is expelled. The liquid is cooled to 30°, the precipitate collected and washed with water at 30°, and then dried at 110°.

L. DE K.

Estimation of Alkaloids. By A. GRANDVAL and H. LAJOUX (*J. Pharm.* [5], 28, 99—103 and 152—156).—*Estimation of Emetine in Ipecacuanha Root.*—The powdered root is extracted with a mixture of alcohol and ether (3 : 8 parts), rendered ammoniacal by the addition of ammonia solution (2 parts), and washed with ether. The ethereal solution is agitated with a little dilute sulphuric acid, separated, and washed until free from alkaloïd. The acid solutions are mixed, rendered alkaline with soda, and again extracted with ether. The ethereal extract, on evaporation, yields the alkaloïd in a nearly pure state.

Such alkaloids as emetine and sparteine are not, as sometimes supposed, destroyed by the dilute acid and alkaline solutions used. Better results are obtained with caustic soda than with carbonates or bicarbonates.

Estimation of Cocaine and Separation of Cocaine and Ecgonine.—The alkaloids from powdered coca leaves are extracted as above, the acid solution being washed free from colouring matters with ether before adding soda. The alkaloids are then neutralised by hydrobromic acid, and powdered potassium bromide added to saturation. The double bromide of cocaine and potassium separates out, and is washed free from ecgonine by means of a cold saturated solution of potassium bromide. The cocaine is then obtained in the crystalline condition by treatment with soda and extraction with ether.

This method becomes general in its application to alkaloids insoluble in ether, provided a suitable solvent is used.

Estimation of Alkaloids with Previous Separation by Potassium Mercury Iodide.—The substance is treated with lead acetate, and extracted with water until the washings give no precipitate with potassium mercury iodide; most of the organic acids present remain as insoluble lead compounds, together with much of the colouring and extractive matter and a large proportion of the proteids. Dilute sulphuric acid is added to the solution obtained, and the lead sulphate filtered off; the alkaloids are then precipitated from the filtrate by means of potassium mercury iodide; variable amounts of albumin and colouring and extractive matters also coming down. After standing some time, the precipitate is collected and treated by one of the following processes:—(1) Potassium cyanide solution, a little soda, and ether or other appropriate solvent are well shaken with the precipitate. The ethereal solution is caused to separate from the emulsion produced, by the addition of a little olive oil, and is then treated with sulphuric acid as above; this acid solution is washed free from adherent olive oil by agitating it with ether, and is then treated as above with soda and ether, so as to recover the alkaloids in the free state. In this process the mercury is dissolved by potassium cyanide, hydriodic acid is eliminated by soda, and the freed alkaloid is dissolved by the immiscible solvent. (2) The decomposition of the precipitate is accomplished by digestion with a slight excess of sodium sulphide, and the extraction of the freed alkaloid is carried out as in the first method. The latter process is considered preferable by the authors.

Liquid alkaloids, in general, cannot be separated by this method, but sparteine forms an exception to the rule.

Atropine is not entirely precipitated by potassium mercury iodide; hence the process cannot be advantageously employed for the extraction of alkaloids from belladonna.

W. T.

Estimation of Resin in Soaps. By J. LEWKOWITSCH (*J. Soc. Chem. Ind.*, 12, 503—508).—The author (Abstr., 1891, 509) has thoroughly investigated Gladding's original silver process for the estimation of resin in fatty acid mixtures; also modifications of the same proposed by Hübl and Stadler and by Grittner and Szilazi. The results, as shown by the tables, prove the method to be utterly untrustworthy. The process recommended by Twitchell (conversion of the fatty acids into ethyl compounds), which may be carried out either gravimetrically or volumetrically, also failed, in the author's hands, to give anything

like an approximate result. This method is, however, comparatively new, and requires further independent investigation (compare Abstr., 1892, 389).
L. DE K.

Qualitative Analysis of Coal-tar Colouring Matters. By A. G. GREEN (*J. Soc. Chem. Ind.*, 12, 3—7).—The author employs a solution of tannin for distinguishing between acid and basic colouring matters, and has also adopted the division into those soluble and those insoluble in water. The chief reagents used are:—A solution containing 10 per cent. of tannin and 10 per cent. of sodium acetate; zinc dust, in conjunction with hydrochloric acid or ammonia; a solution containing 1 per cent. of chromic acid (for basic colours); a solution containing 1 per cent. of chromic acid, or potassium dichromate and 5 per cent. of sulphuric acid (for acid colours).

When the sample is soluble in water, its behaviour towards tannin is first ascertained, and the liquid is next reduced by zinc dust and hydrochloric acid. A drop of the now colourless liquid is put on to filter paper, and mixed with a drop of the chromic acid solution. This will cause different colorations, according to the nature of the dye, as indicated by reference to the author's tables.

Insoluble colours are treated with weak aqueous soda, and reduced by zinc dust and ammonia. If the soda refuses to dissolve the colour, alcohol must be used. The solution is then further examined, as directed in the special table.
L. DE K.

Albumin and Sugar in Urine. By BENNO-LAQUER (*J. Pharm.* [5], 28, 134—135).—The clear, filtered urine is heated to boiling, and a tenth of its volume of nitric acid added in one operation. If a flocculent and persistent precipitate forms, the urine is albuminous. To the clear solution, cooled and filtered if necessary, 10—20 drops of Almen's solution is added, and the test heated again for 1—2 minutes. Sugar is indicated by a dark brown coloration.

Almen's solution is prepared by dissolving 4 grams of Rochelle salt in 100 parts of a 10 per cent. solution of soda, and digesting this liquid with 2 grams of bismuth subnitrate until mostly dissolved. This solution indicates glucose more readily than Fehling's solution, and is not affected by uric acid or creatinine.
W. T.

Valuation of Hide Clippings for Glue making. By F. GANTTER (*Zeit. anal. Chem.*, 32, 413—415).—For this purpose, it is necessary to estimate the insoluble mechanical impurities, the gelatin, and the soluble constituents which are not gelatin. The first are ascertained by boiling the substance with water until dissolved, and allowing the solution to clarify, when sand, &c., will subside, and fat will rise to the surface. The clear solution from 100 grams of the substance (boiled with 1 litre of water to which a few drops of soda solution have been added) is made up to 2 litres, and 20 c.c. of it evaporated, dried at 105°, weighed, and incinerated. This gives the total amount of ash-free organic matter. Another 10 c.c., diluted with 30 c.c. of water and neutralised with acetic acid, is treated with tannin solution until no further precipitation takes place, and then made up to

100 c.c. The excess of tannin is removed from the filtrate by hide powder, and the amount of organic matter in 50 c.c. is then ascertained as above. The gelatin can be calculated from the difference.

M. J. S.

Discrimination between Genuine and Exhausted Ginger. By B. DYER and J. F. H. GILBARD (*Analyst*, 18, 197—200).—The authors recommend taking the alcoholic extract, after first extracting the sample with ether. In genuine gingers, it ranges from 2.1 to 3.8 per cent.; in the exhausted samples, from 0.8 to 1.4 per cent. They also attach great value to the constitution of the ash, which, in genuine samples (excluding sand) ranges from 3.1 to 4.1 per cent., whilst, in exhausted samples, it is only 1.1 to 2.3 per cent. The ash soluble in water is especially important, as, in genuine samples, it ranges from 1.9 to 3 per cent., whilst, in exhausted samples, it is 0.2 to 0.5 per cent.

The authors, whilst not denying that some samples of ginger may be mixed with a considerable amount of exhausted ginger without fear of detection, still hope that their process will be useful to prove a flagrant adulteration of the drug.

L. DE K.

Estimation of Fibre in Foods by means of the Centrifugal Apparatus. By W. THÖRNER (*Chem. Zeit.*, 17, 394—395).—About 1 gram of the sample is freed from fatty matter by means of ether. The operation is conducted in a special tube, which is rotated for a few minutes in the author's centrifugal machine. The ether can then be poured off without any loss of insoluble matter. After the layer of ether has been removed, the tube is filled with dilute sulphuric acid, and placed in boiling water for 30 minutes to cause the starchy matter to dissolve. The insoluble matter takes a long time to settle, but when the tube is placed in the machine and rotated for four minutes at a speed of 2000 revolutions per minute, the residue completely separates as a compact mass at the bottom of the tube, and the supernatant liquid may then be poured on to a weighed filter. The insoluble matter is then treated with 40 c.c. of hot water for 10 minutes, and the tube is once more whirled. After pouring off the washings, the fibre is heated with dilute aqueous potash to remove nitrogenous matters and again whirled.

The fibre is finally transferred to the filter, well washed with water, alcohol, and ether, and dried to constant weight. It should, of course, be tested for mineral matter. The process gives very concordant results, and with a moderate-sized machine, eight estimations may be completed within three or four hours.

L. DE K.

Estimation of Silk in Fabrics. By F. W. RICHARDSON (*J. Soc. Chem. Ind.*, 12, 426—431).—The author recommends the following process:—25 grams of crystallised nickel sulphate is dissolved in 500 c.c. of water; the nickel is then completely precipitated as hydroxide by sodium hydroxide, and thoroughly washed. The precipitate is rinsed into a 250-c.c. flask with 125 c.c. of water; the flask is then filled to the mark with ammonia of 0.88 sp. gr., and well

shaken. Silk is rapidly dissolved in this solution, even in the cold, whilst cotton and wool are practically insoluble.

To dissolve silk from plush, a 10 minutes' boiling under a reflux condenser is required. In the cold, cotton loses 0.4 per cent.; on boiling, 0.8 per cent. of its weight.

L. DE K.

INDEX OF AUTHORS' NAMES.

ABSTRACTS. 1893. Parts I & II.

And also to Transactions, 1893 (marked TRANS.); and to such papers as appeared in the Proceedings during the Session 1892—1893 (Nos. 115 to 127; Nov., 1892, to July, 1893), but not in Transactions (marked PROC.).

A.

Abegg, R., diffusion in aqueous salt solutions, ii, 265.
 Abel, J., condensation of formaldehyde with naphthols, i, 172.
 Abel, J. J., and A. Muirhead, carbamic acid in the urine after ingestion of calcium hydroxide, ii, 333.
 Abend, L. See Geigel.
 Abenius, P. W., paradiazine derivatives, i, 374.
 Abenius, P. W., and H. G. Söderbaum, aromatic tetraketones, i, 169.
 Adolphi, W., chebolic acid, i, 212.
 Adrian, C., influence of dividing the daily nutriment on the metabolism of the dog, ii, 383.
 Aglot, E., estimation of precipitates by an optical method, ii, 294.
 Agrestini, A., hepatic mineral water and mud of the Valle del Gallo, ii, 175.
 Ahrens, F. B., sparteïne, i, 232.
 Aignan, A., influence of temperature on the rotatory power of liquids, ii, 354.
 Aladern. See D'Aladern.
 Alberti and Hempel, estimation of inorganic constituents in sugars, ii, 51.
 ——— estimation of nitrogen in nitrates, ii, 42.
 ——— estimation of nitrogen in sodium nitrate, ii, 87.
 Alén, J. A., preservation of milk for analysis, ii, 308.
 Alexander, volumetric estimation of lead, ii, 599.
 Alexandroff, P., and N. Saytzeff, isoerucic acid, i, 549.
 Alkemade. See Van Rijn Van Alkemade.
 VOL. LXIV. ii.

Allaire, H. See Rousseau.
 Allen, A. H., volumetric estimation of alkaloïds, ii, 252.
 Allen, L. S., iodoso- and iodoxy-derivatives of metanitropariodobenzoic acid, i, 578.
 Altschul, M., critical constants of some organic compounds, ii, 446.
 Alvisi, U., action of phenylhydrazine on ethylene chlorhydrin, i, 639.
 — relation between the periodic classifications of L. Meyer and Mendeléeff, ii, 513.
 — specific gravities of the elements in the periodic system, ii, 513
 — the camphor group, i, 660.
 A magat, E. H., laws of the expansion of liquids compared with those relating to gases, and the form of the isothermals for liquids and gases, ii, 152.
 Amerman, G. L. See Chittenden.
 Ampola, G. See Oddo.
 Anthor, C., and J. Zink, analysis of lard, ii, 101.
 Anderlini, F., action of diamines on cantharidin, i, 483.
 — derivatives of cantharidin, i, 483.
 Anderlini, F., and E. Borisi, condensation of ethylic formate and succinate, i, 192.
 André, G. See Berthelot.
 Andreocci, A., derivatives of urethane, i, 128.
 — new isomeride of santonin and santonous acid, i, 526.
 Andrews, T., electrochemical effects on magnetising iron, ii, 404.
 — passive state of iron and steel ii, 16.
 Angeli, A., action of iodic acid on malonic acid: triiodoacetic acid, i, 307.

- Angeli, A., action of nitric and nitrous acid on certain organic substances, i, 196.
- action of nitrous acid on isosafrole, i, 261.
- action of nitrous acid on ketamines, i, 570.
- affinity coefficients of some pyrrol-ine and indole acids, i, 42.
- compounds containing the group $C_2N_2O_2$, i, 355.
- novel conversion of camphor into camphoric acid, i, 277.
- oxidation of substances containing the group $C_2N_2O_2$, i, 310.
- Angeli, A., and P. Bartolotti, action of nitrous acid on isoapiole, i, 263.
- Angeli, A., and G. Boeris, influence of electrolytic dissociation on the decomposition of ammonium nitrite in aqueous solution, ii, 155.
- Anschütz, R., Heintz's glycolide, i, 306.
- preparation of pure chloroform from salicylide-chloroform, i, 121.
- salicylide, i, 165.
- Anschütz, R., and F. Biernaux, diglycollic acid and thiodiglycollic acid, i, 191.
- Anschütz, R., and W. O. Emery, perchlorethyl chloroformate and trichloromethyl trichloracetate, i, 188.
- Anschütz, R., and W. Montfort, formation of phoronic acid from phorone, i, 304.
- Anschütz, R., and E. Parlato, ethylic oxomalonate, i, 193.
- Anthoine, crystalline dihydrochloride from eucalyptus oil, i, 223.
- Antoine, C., tensions of vapours, ii, 9.
- Antony, U., action of chlorine and carbonic oxide on iridium, ii, 214.
- composition of the precipitate obtained with hydrogen sulphide in solutions of potassium iridichloride, ii, 379.
- lithium iridichloride and iridium bisulphide, ii, 380.
- Antony, U., and P. Donnini, manganoous sulphide, ii, 527.
- Antony, U., and L. Niccoli, separation of the metals precipitated by hydrogen sulphide in acid solutions, ii, 192.
- Antushevitch, J. A., analysis of bees'-wax by Hübl's method, ii, 198.
- Antushevitch, J. See Sabanéeff.
- Appleyard, J. R. See Frankland.
- Araki, T., action of phosphorus and arsenious oxide on the animal organism, ii, 136.
- Araki, T., β -hydroxybutyric acid in the organism, ii, 428.
- Archbutt, L., estimation of silica in clay, ii, 300.
- Armstrong, H. E., note on optical properties as indicative of structure, *Proc.*, 1893, 57.
- the conditions determinative of chemical change, *Proc.*, 1893, 145.
- the nature of depolarisers, *Proc.*, 1893, 148, 188.
- the origin of colour. Part V. Coloured hydrocarbons and fluorescence, *Proc.*, 1892, 189.
- the origin of colour. Part VI. Azobenzene, *Proc.*, 1892, 194.
- the origin of colour (including fluorescence). Part VII. The phthal-eins and fluoresceins, *Proc.*, 1893, 52.
- the origin of colour. Part VIII. The limitation of colour to truly quinonoid compounds. Change of colour as indicative of structure, as in the case of alizarin, *Proc.*, 1893, 55.
- the origin of colour. Part IX. Note on the appearance of colour in quinoline derivatives and of fluorescence in quinine, *Proc.*, 1893, 63.
- Armstrong, H. E., and F. S. Kipping, studies on the terpenes and allied compounds. The formation of ketones by the interaction of camphor and agents such as sulphuric acid and zinc chloride, *Trans.*, 75.
- Armstrong, H. E., and G. H. Robertson, the Planté lead | sulphuric acid | lead peroxide cell from a chemical standpoint, ii, 4.
- Armstrong, H. E., and W. P. Wynne, ortho-, para-, and peri-disulphonic derivatives of naphthalene, *Proc.*, 1893, 166.
- the Griess-Sandmeyer interactions and Gattermann's modifications thereof, *Proc.*, 1892, 199.
- Arnaud and Charrin, physiological action of cinchonamine sulphate, ii, 223.
- Arnold, C., and K. Wedemeyer, estimation of nitrogen in urine, ii, 343.
- Kjeldahl's method of estimating nitrogen, ii, 88.
- Spica's process for the estimation of phosphoric acid, ii, 299.
- Arrhenius, S., determination of the electrolytic dissociation of salts by means of solubility experiments, ii, 364.
- electrolysis of alkali salts, ii, 441.
- Arthus, M., and A. Huber, difference between formed and unformed ferments, ii, 31.

- Arthus, M., and A. Huber, solutions of fibrin, i, 743.
 Asbóth, A. v., action of hydrogen peroxide on starch, i, 384.
 — volumetric estimation of sulphuric acid in sulphates, ii, 240.
 Aschan, O., acids from Baku petroleum, i, 209.
 — bromocamphoric anhydride and camphoric acid, i, 598.
 — hexahydrobenzoic acid, i, 209.
 — hydrobenzoic acids, i, 33.
 Aschoff, K. See Jannasch.
 Askenasy, P., and V. Meyer, iodoso-compounds, i, 506.
 Aston, Miss E. See Ramsay.
 Auerbach, F., new collidine, i, 175.
 — pipercolinecarboxylic acid, i, 176.
 Aulard, A., raffinose and its decomposition products, i, 683.
 Autenrieth, W., potassium ferrocyanide: detection of hydrocyanic acid in presence of ferrocyanides, ii, 393.
 Auwers, K., pentanetetracarboxylic acid: synthesis of pentamethylene derivatives, i, 253.
 Auwers, K., and H. Kauffmann, stereoisomeric derivatives of the symmetrical dimethylglutaric acids, i, 72.
 Auwers, K., and H. Schnell, camphoric acid, i, 525.
 Auwers, K., and M. Siegfeld, benzileoximes, i, 354.
 Ayres, E. F. See Yeates.

B.

- Babbitt, H. C., Emmerton's process for the estimation of phosphorus, ii, 553.
 — precipitation of ammonium phosphomolybdate in the presence of arsenic, ii, 236.
 Bach, A., assimilation of carbonic anhydride by chlorophyllous plants, ii, 483.
 — condensation of carbonic anhydride under the influence of sunlight, ii, 484.
 Bachofen, C. See Heumann.
 Bachofen, F. See Lunge.
 Bäckström, H., estimation of arsenic, ii, 299.
 Baeyer, A., hydro-derivatives of benzene, i, 255.
 — orientation in the terpene series, i, 359, 722.
 — synthesis of dihydrocymene, i, 258.
 Baeyer, A., and V. Villiger, hexahydroisophthalic acid, i, 713.
 Bagard, H., thermoelectric phenomena between two electrolytes, ii, 202.

- Baisch, K., the carbohydrates of normal urine, ii, 542.
 Baker, H. B., the influence of moisture on promoting chemical action, *Proc.*, 1893, 129.
 Baker, J. L. See Ling.
 Balbiano, L., oxidation of camphoric acid, i, 174.
 — phenylethyldimethylpyrazole, i, 672.
 — platopyrazole compounds, i, 674.
 Balbiano, L., and G. Marchetti, synthesis of homologues of 1-phenylpyrazole, i, 672.
 Balbiano, L., and O. Severini, some acids of the pyrazole series, i, 673.
 Baldracco, G. See Fileti.
 Balestra, E., action of potassium iodide or sodium thiosulphate on mercurammonium salts, ii, 278.
 — new mercurammonium salts, i, 304.
 Balke, P., xanthine derivatives, i, 535.
 Balland, pre-existence of gluten in wheat, ii, 292.
 Baly, E. C. C., separation and striation of rarefied gases under the influence of the electric discharge, ii, 253.
 Bamberger, E., action of diazobenzene on β -ketonic acids, i, 156.
 — constitution of five-membered rings, i, 426.
 — imidazoles, i, 432.
 — valency of nitrogen in pyrroline, i, 727.
 Bamberger, E., and B. Berlé, addition of chloral to quinoline bases and benzimidazoles, i, 438.
 — behaviour of the 2'-methyl group in benzimidazoles, i, 435.
 — dibenzilyldiamidoethylene, i, 200.
 — opening of the benzimidazole ring, i, 437.
 Bamberger, E., and F. Chattaway, chrysene, i, 593.
 — picene, i, 594.
 Bamberger, E., and W. Dieckmann, tetrahydroisoquinoline, i, 528.
 Bamberger, E., and K. Landsteiner, behaviour of diazobenzene towards potassium permanganate, i, 327.
 Bamberger, E., and W. Lodter, dihydronaphthalene and its derivatives, i, 591.
 Bamberger, E., and J. Lorenzen, constitution and formation of benzimidazoles, i, 433.
 — formazyl methyl ketone, i, 157.
 Bamberger, E., and F. Meimberg,

- direct conversion of aniline into nitrobenzene, i, 323.
- Bamberger, E., and L. Seeberger, constitution of dicyanodiamide, i, 494.
- Bamberger, E., and H. Sternitzki, dihydromethylketole, i, 520.
- Bamberger, E., and L. Storch, behaviour of diazobenzene towards potassium ferricyanide, i, 326.
- Bamberger, E., and E. Wheelwright, action of diazobenzene on ethylacetoacetate, i, 84.
- Bamberger, E., and E. A. Zumbro, dihydromethylketole, i, 468.
- Bancroft, W. D., electromotive force of oxidation cells, ii, 58.
- Barad, D. See Bischler.
- Barbier, C., licarhodol from licareol, i, 544.
- Barbier, P., constitution of licareol, i, 496.
- constitution of rhodinol, i, 661.
- derivatives of licareol, i, 495.
- dextrogyrate licareol, i, 661.
- geraniol, i, 664.
- licarene from licareol, i, 493.
- Barillot, E., impurities in crude methyl alcohol, ii, 196.
- Baroni, G., determination of molecular weights by Beckmann's method, ii, 511.
- Barthe, L., analysis of quinine sulphate, and estimation of quinine in presence of other cinchona alkaloïds, ii, 199.
- synthesis with the aid of ethylic cyanoacetate and ethylic cyanosuccinate, i, 305.
- volumetric estimation of alkaloïds, ii, 146.
- Barthe and Falières, complete elimination of barium from strontium salts, ii, 209.
- Barthel, G., light petroleum burner, ii, 368.
- Bartolli and Stracciati, specific heat of water, ii, 443.
- Bartolotti, P. See Angeli.
- Baruch, J., constitution of behenolic acid, i, 551.
- Baruch, J. See also Holt.
- Barus, C., and E. A. Schneider, behaviour of solid colloidal silver towards the electrical current, ii, 314.
- Baskerville, C. See Corse.
- Bau, A., estimation of isomaltose in worts, ii, 601.
- Baubigny, H., and E. Péchard, dissociation of chrome alum, ii, 73.
- Bauch, E. See Töhl.
- Bauer, R. W., sugar from pear pectose, i, 248.
- Baumann, A., estimation of antimonious oxide, ii, 90.
- estimation of arsenious acid, ii, 90.
- estimation of hydrogen and barium peroxides, ii, 86.
- gas-volumetric alkalimetry, ii, 91.
- gas-volumetric estimation of iodine and acids, ii, 87.
- gas-volumetric estimation of potassium ferricyanide, ii, 98.
- Baumann, E., excretion of ethereal hydrogen sulphates, ii, 290.
- oxidation of the two trithioacetaldehydes, i, 684.
- Baumann, E., and G. Walter, hydrolysis of sulphones, sulphone-sulphinic acids, and sulphinolactones, i, 458.
- Baumeister, W., preparation of hydroxyxanthenes from the salols of polyhydric phenols, i, 218.
- Bayard, C. See Causse.
- Bayer, A., direct estimation of potassium and sodium by means of tartaric acid, ii, 598.
- Bayer, R. See Claus.
- Bayley, W. S., augite and plagioclase in a Minnesota gabbro, ii, 78.
- Beadle, C. See Cross.
- Béchamp, A., absence of spontaneous inversion of cane sugar in aqueous solution at the ordinary temperature, i, 547.
- gum arabic, i, 294.
- Beck, C. orthonitrobenzyl derivatives, i, 415.
- Beck, C. R. See Shenstone.
- Beckencamp, J. See Claus.
- Becker, A. See Sachse.
- Beckmann, E., benzylbenzaldoxime, i, 706.
- Beckmann, E., and E. Fellrath, action of phenylcarbimide on benzylbenzaldoxime, i, 203.
- Beckmann, E., and A. Köster, basic bye-product obtained by benzylating acetoxime, i, 464.
- hydroximido-derivatives: beziloximes, i, 474.
- Béhal, A., and C. Choay, creosotes and guaiacol, i, 320.
- derivatives of chloral, i, 301.
- Behrend, R., electrometric analysis, ii, 387.
- Behrend, R., and J. Schmitz, action of nitric acid on acetone, i, 303.
- Beijerinck, M. W., butylic alcoholic fermentation and the butylic ferment, ii, 586.
- Beill, A., influence of temperature on the formation of ozone, ii, 317.

- Bel. See Le Bel.
 Bell. See De Bell.
 Bemmelen. See Van Bemmelen.
 Benedikt, H., β -hydrindone and its derivatives, i, 587.
 Benedikt, R., analysis of beeswax, ii, 397.
 Benedikt, R., and H. Strache, analyses of ethereal oils, ii, 560.
 Benno-Laquer, detection of albumin and sugar in urine, ii, 610.
 Berg, A., chloramines, i, 497.
 — chlorine derivatives of propylamines, benzylamines, aniline, and paratoluidine, i, 296.
 Berger, R. See Möhlau.
 Berkeley, W. N., paranthrite from Clay Co., N. Carolina, ii, 287.
 Berkenheim, A., crystalline substance from *Santalum praesii*, i, 666.
 Berlé, B. See Bamberger.
 Bernheim, A., exudations and transudations, ii, 334.
 Bernthsen, A., metamidodialkylorthotoluidines, i, 409.
 — metamidodialkylorthotoluidines and their conversion into methylene-blue dyes, i, 75, 77.
 Bertels, A., influence of chloroform on peptic digestion, ii, 217.
 Berthelot, absorption of atmospheric nitrogen by microbes, ii, 83.
 — absorption of free nitrogen by plants, ii, 138.
 — heat of combustion of camphors, ii, 108.
 — heat of combustion of glycollic acid, ii, 6.
 — metallic aërolite, ii, 326.
 — the nitrogen-fixing micro-organisms, ii, 429.
 Berthelot and André, the organic constituents of soils, ii, 341.
 Berthelot and Matignon, glyoxylic or dihydroxyacetic acid, ii, 6.
 — heat of combustion of chlorine compounds, ii, 5.
 — heats of combustion of gaseous hydrocarbons, ii, 444.
 Berthelot, D., electrical conductivities of phosphoric acid and of alkali phosphates, ii, 357.
 Bertin-Sans, H., and J. Moitesier, action of carbonic oxide on reduced hæmatin and hæmochromogen, i, 448.
 — oxyhæmatin, reduced hæmatin, and hæmochromogen, i, 447.
 Bertram, J., and H. Walbaum, pine needle oils, i, 659.
 Bertrand, G., essential oil of niaouli, i, 523, 727.
 Bertrand, G., xylose, i, 248.
 — zincoxides of alkaline earths, ii, 118.
 Bertrand, G., and G. Poirault, colouring matter of pollen, ii, 139.
 Besson, A., carbon chloriodide, i, 185.
 — decomposition of chloroform in the presence of iodine, i, 242.
 Bevad, L., ethereal salts of nitrous acid, i, 382.
 — synthesis of mononitroparaffins, i, 242.
 Bevan, E. J. See Cross.
 Bial, M., diastatic action of the serum of blood and lymph, ii, 333.
 — diastatic ferment in blood, ii, 581.
 Biernacki, E., influence of antiseptics on fermentation, ii, 32.
 Biernaux, F. See Anschütz.
 Biétrix, A., bromogallic acid and its derivatives, i, 583.
 — derivatives of gallic acid, i, 343.
 — dibromogallic acid and its salts, i, 269, 343.
 — triacetyldibromogallic acid and tribenzoyldibromogallic acid, i, 643.
 Bigelow, W. D. See MacElroy.
 Biginelli, P., aldureïdes of ethylic acetoacetate and ethylic oxalacetate, i, 645.
 Bigot, A., some derivatives of glycerol, i, 3.
 Billeter, O., penta-substituted dithiobiurets, i, 575.
 Biltz, H., action of chloral on benzene in the presence of aluminium chloride, i, 718.
 — explosives, ii, 409.
 — the aluminium chloride synthesis, i, 718.
 — vapour density of halogen halides at low temperatures, ii, 65.
 Binz, A. See Wallach.
 Birmann, E., alkaloïds of *Cordyialis nobilis*, i, 446.
 Bischler, A., new synthesis of pyrazole derivatives, i, 44.
 Bischler, A., and D. Barad, phenometadiazine, i, 47.
 Bischler, A., and E. Burkart, phenometadiazine derivatives, i, 530.
 Bischler, A., and P. Fireman, 2':3'-diphenylindoles, i, 519.
 Bischler, A., and F. J. Howell, phenometadiazine derivatives, i, 531.
 Bischler, A., and B. Napieralski, new synthesis of isoquinoline, i, 608.
 Bischler, A., and W. Oser, new synthesis of pyrazole derivatives, i, 610.
 — phenometadiazine derivatives, i, 609.
 Bischoff, C. A., piperazine group, i, 54.

- Bischoff, C. A., and A. Hausdörfer, acidoxyl-derivatives of diphenylethylenediamine and ditolyethylenediamine, i, 78.
- derivatives of α - and β -naphthylamines containing asymmetrical nitrogen and carbon atoms, i, 98.
- Bischoff, C. A., and C. Trapezon-janz, monoketopiperazines, i, 53.
- Bischoff, C. A., and P. Walden, anilides and toluidides which exist in two modifications, i, 511.
- application of the dynamical hypothesis to keto-acid derivatives, i, 499.
- glycollide and its homologues, i, 250.
- Bistrzycki, A. See Liebermann.
- Bitté, B. v., composition of the ripe husks of capsicum, ii, 546.
- Bizzarri, D., carbazacridines: oxidation of phenylcarbazacridine, i, 417.
- Blackshear, C. C., sulphonephthal-eins, i, 94.
- Bladin, J. A., oxidation of azimido-toluene, i, 375.
- Blank, A., action of diazobenzene chloride on α -hydroxyvutic acid, i, 341.
- Blank, P., derivatives of trimethylene chlorobromide, i, 8.
- Blattner, N. G., estimation of free alkali in commercial hypochlorites, ii, 91.
- Blau, F., constitution of nicotine, i, 375, 489.
- Bleibtreu, L. See Wendelstadt.
- Bleibtreu, M., and L. Bleibtreu, method of estimating the volume of the corpuscles of the blood, ii, 331.
- Bloch. See Schlagdenhauffen.
- Blomstrand, C. W., complex acids containing heptavalent iodine, ii, 122.
- Bloxam, W. P., the sulphides and polysulphides of ammonium, PROC., 1893, 178.
- Blümcke, A., labile conditions of equilibrium in salt solutions, ii, 447.
- Bodenstein, M., and V. Meyer, decomposition of gaseous hydrogen iodide by heat, ii, 369.
- Bodewig, A. See Paal.
- Bodländer, G., cobaltiferous chalybite from Neukirchen, ii, 129.
- composition of melilite, ii, 174.
- Bödtker, E., estimation of urea, ii, 146.
- Boeris. See Angeli.
- Böttcher, O., estimation of nitric nitrogen, ii, 145.
- estimation of nitrogen by Kjeldahl's method, ii, 144.
- Boiret, H., and G. Paturel, employment of ferrous sulphate in agriculture, ii, 142.
- Boisbaudran. See De Boisbaudran.
- Bokorny, T., assimilation of formaldehyde by green plant cells, ii, 32.
- Bombien. See Hiller-Bombien.
- Bondzynski, S., detection of mercury in urine, ii, 438.
- Sjöqvist's method of estimating the free hydrochloric acid in gastric juice, ii, 433.
- Bone, W. A., studies on the indoxazen reaction, TRANS., 1346.
- Bone, W. A. See also Meyer.
- Borg, F. See Villiers.
- Borisi, E. See Anderlini.
- Bornemann, G., aluminium apparatus in the laboratory, ii, 162.
- Bornträger, A., use of potassium hydrogen tartrate in volumetric analysis, ii, 144.
- Bornträger, H., rapid reduction of potassium platinochloride, ii, 284.
- separation of iron from aluminium, ii, 304.
- Bossel, F. See Graebe.
- Bossi, A. See Nietzki.
- Bothamley, C. H., distribution of acids and bases in a solution containing calcium, magnesium, carbonic acid, and sulphuric acid, and on the composition of mineral waters, TRANS., 696.
- the mineral waters of Askern, Yorkshire, TRANS., 685.
- Bouchardat, G., action of acetic anhydride on linalol, i, 544.
- Bouchardat, G., and J. Lafont, action of sulphuric acid on citrene, i, 223.
- Bouchardat, G., and Olivero, essence of eucalyptus, i, 726.
- action of acetic and formic acids on terebenthene, i, 358.
- Bouillot, J., alkaloids in cod liver oil, ii, 290.
- Boulenger. See Le Boulenger.
- Bourquelot, E., inulase and the indirect alcoholic fermentation of inulin, i, 497.
- occurrence of trehalose in fungi, ii, 337.
- trehalase, a ferment for trehalose, i, 451.
- Boutmy, H. See Nencki.
- Bouveault, L., constitution of camphor and oil of turpentine and of their principal derivatives, i, 276.
- hydrolysis of aromatic nitriles, i, 541.
- liquid isomeride of hydrocamphene, i, 523.
- preparation of triphenylacetone nitrile and triphenylcarbinol, i, 589.

- Bouveault, L., so-called hydrazone of cyanacetone, i, 571.
- Boyanus, A., allylmethylhexylcarb-inol, i, 544.
- Brancovici, E. See Haller.
- Brandenburg, H., abnormal electro-motive force of mercury, ii, 356.
- Brandl, J., absorption and secretion from the stomach, ii, 581.
- Brandl, J., and H. Tappeiner, fluorine compounds in the organism, ii, 23.
- Braunschweig, R. See Brühl.
- Bréal, E., assimilation of nitrogen by plants, ii, 590.
- Bredig, G., electrolytic dissociation of water, ii, 448.
- molecular weight of potassium per-sulphate, ii, 572.
- Breisacher, L., amount of albumin required for the human body, ii, 328.
- Bremer, G. J. W., apparatus for ex-tracting the gases dissolved in water, ii, 432.
- bottle for taking samples of water at known depths, ii, 432.
- Breyer, T., and H. Schweitzer, es-timation of potassium by the Lindo-Gladding process, ii, 436.
- Broche, C., tribromacetonitrile, i, 289.
- Brochet, A., condensation of hydro-carbons of the benzene series with those of the ethylene series, i, 635.
- Brochet, A., and P. le Boulenger, condensation of aliphatic alcohols with aromatic hydrocarbons, i, 634.
- Brodie, T. G. See Halliburton.
- Brögger, W. C., sundite, a new mineral from Oruro, Bolivia, ii, 382.
- Brown, A. Crum, and J. Walker, electrolytic synthesis of bibasic acids, i, 394.
- Brown, H. T., and G. H. Morris, a contribution to the chemistry and physiology of foliage leaves, TRANS., 604.
- Brown, J., difference of potential at the contact of mutually reacting liquids, ii, 149.
- electrolytic conductivity and dis-sociation, ii, 59.
- voltaic cells with fused electrolytes, ii, 403.
- Browning, P. E., detection of strontium in presence of calcium, ii, 47.
- influence of nitric acid and nitro-hydrochloric acid on the precipitation of barium sulphide, ii, 552.
- quantitative separation of barium and strontium by the action of amyl alcohol on their bromides, ii, 241.
- Browning, P. E., quantitative separa-tion of strontium and calcium nitrates by means of amyl alcohol, ii, 241.
- Browning, P. E. See also Gooch.
- Bruck, P., di-iodides of tetrolic and acetylenedicarboxylic acids, i, 397.
- Brühl, J. W., ethereal salts of cam-phoric acid, i, 423.
- spectrochemistry of nitrogen, ii, 254.
- Brühl, J. W., and R. Braunschweig, asymmetrical dicarboxylic acids, i, 251.
- ethereal salts of pyrotartaric acid, i, 307.
- terpenes and their derivatives, i, 277.
- Brunck, O., formation of ozone at high temperatures, ii, 454.
- Brunck, R., thienylindole, α -naphth-indole, and some bromo-derivatives of indoles, i, 168.
- Brunlechner, A., descloizite from the Obir, ii, 577.
- Brunner, H., and H. Leins, separa-tion of theobromine and caffeine, ii, 608.
- Brunner, K., dimolecular propionic cyanide: ethyltartronic acid, i, 553.
- synthesis of isomalic acid, i, 145.
- Bruttini, A., colorimetric estimation of small quantities of uranium in minerals, ii, 555.
- Bruyn. See Lobry de Bruyn.
- Bucherer, A. H., formation of alu-minium sulphide, ii, 169.
- Buchner, E., synthesis of pyrazole de-rivatives by means of ethylic diazo-acetate, i, 429.
- Buchner, E., and H. Dessauer, 5-phenylpyrazole, i, 282.
- Buchner, E., and M. Fritsch, 4-phenylpyrazole, i, 281.
- preparation and derivatives of pyrazole, i, 432.
- pyrazole-3:4:5-tricarboxylic acid, i, 432.
- Buchner, E., and A. Papendieck, pyrazole-3:5-dicarboxylic acid, i, 431.
- pyrazoline-3:5-dicarboxylic acid, i, 430.
- Buchner, E., and H. Witter, pyr-azolone-3:4:5-tricarboxylic acid, i, 431.
- Buchner, G., estimation of the hard-ness of water by means of soap, ii, 347.
- Hübl's process for testing wax, ii, 351.
- Bucket, M., examination of tartaric and citric acids for lead, ii, 557.

- Büchner, O., trichloropyruvic acid, i, 308.
- Bülow, K., action of amides on benzaldehyde, i, 712.
- Büttner, B. See Claus.
- Bugarszky, S., conditions of chemical equilibrium, ii, 450, 566.
- Bugarszky, S. See also Liebermann.
- Buisman, H. J., and A. R. Van Linge, phosphates from Florida, ii, 419.
- Bujard, A. See Klinger.
- Bunge, N. A., electrolysis of substituted organic acids, i, 640.
- Burkart, E. See Bischler.
- Burls, F. B., R. E. Evans, and C. H. Desch, formation of hydrocyanic acid by the action of nitric acid on sugar, &c., i, 617.
- Burls, F. B. See also Meldola.
- Burns, P. S., reactions of dimolecular nitriles, i, 314.
- C.**
- Cairola, E. See Fileti.
- Caldwell, G. C., estimation of sugar in tomatoes, ii, 555.
- Camerer, W., Hüfner's method of estimating urea, ii, 560.
- metabolism in a child 14 months old, ii, 476.
- Camichel, C., absorption of light by liquid bromine, ii, 561.
- Campbell, E. D., estimation of phosphorus in iron in presence of arsenic, ii, 554.
- Cannepin and Van Eijk, titration of morphine in opium, ii, 607.
- Cannizzaro, S., Klein's view of the constitution of santonin, i, 364.
- Cannizzaro, S., and P. Gucci, derivatives of photosantonin acid, i, 665.
- Cantalupo, A. See Fileti.
- Cantor, M., chemistry of secondary batteries, ii, 150.
- Carhart, H. S., a 1-volt standard cell, ii, 562.
- Carlsgren, O., and P. T. Cleve, some platinum ammonium compounds, ii, 127.
- Carnot, A., estimation of manganese by oxydimetric methods, ii, 497.
- estimation of manganese oxides by means of hydrogen peroxide, ii, 497.
- estimation of phosphorus in iron and steel, ii, 235.
- estimation of phosphorus in soil, ii, 489.
- Caro, N., trihydroxyaurin from catechol, i, 274.
- Carpenter, F. B., analysis of tobacco cured by the leaf cure, on wire, and by the stalk process, ii, 547.
- Carr, F. H. See Dunstan.
- Carrara, G., isomeric thetines, i, 633.
- molecular weight and refractive power of hydrogen peroxide, ii, 163.
- Cash, J. T., and W. R. Dunstan, action of nitrites on muscle, ii, 384.
- Caspari, R., preparation of perchloric acid, and estimation of potassium in presence of non-volatile acids, ii, 390.
- Cassal, C. E., estimation of insoluble fatty acids, ii, 308.
- Cassirer, H., orthocyno- and ortho-nitro-benzyl chloride, i, 16.
- Catheart, W. R., jun., oximes of symmetrical benzophenones, i, 97.
- Catheart, W. R., jun., and V. Meyer, indoxazen group, i, 94.
- Catlett, C. See Clarke.
- Causse, H., basic gallate of bismuth, i, 643.
- Causse, H., and C. Bayard, pyrogallol antimonites, i, 75.
- Cazeneuve, P., action of alkali alkyl oxides on camphoric anhydride and other anhydrides, i, 362.
- constitution of camphor, i, 598.
- constitution of gallic blue and tannin indigo, i, 510.
- derivatives of amethylcamphonitroketone, i, 109.
- gallanilide and its triacetyl and tribenzoyl derivatives, i, 412.
- metallic derivatives of gallanilide, i, 638.
- propylamidophenol and its acetyl derivatives, i, 199.
- propylamidophenol from camphor, i, 152.
- tinctorial properties of amethylcamphonitroketone, i, 110.
- Cerkez, S. G., rotatory power of salts of quinic acid, i, 644.
- Chalmot. See De Chalmot.
- Chambrier. See De Chambrier.
- Chance, F., dipropylamidoacetic acid, i, 554.
- dipropylcarbamide and dipropylthiocarbamide, i, 253.
- dipropylcyanamide and dipropylcarbodiimide, i, 297.
- preparation and purification of the propylamines, i, 249.
- tripropylamidoacetic acid, i, 554.
- Chapman, A. C., the essential oil of hops, *Proc.*, 1893, 177.
- Charrin. See Arnaud.
- Chatelier. See Le Chatelier.
- Chattaway, F. See Bamberger.

- Chattaway, F. D., phenylnaphthalenes. I. *α*-Phenylnaphthalene, *TRANS.*, 1185.
- Chavanne, L. See Guye.
- Chenel, L., estimation of nitrogen in nitrates and nitro-compounds by Kjeldahl's method, ii, 87.
- Cherix, C., volumetric estimation of sulphuric acid in alkali sulphates, ii, 89.
- Chiaromonte, T., estimation of tannin in wine, ii, 311.
- Chittenden, R. H., and G. L. A. Meriman, artificial and natural digestion, ii, 423.
- Choay, C. See Béhal.
- Christensen, O. T., reactions with ammonia at low temperatures, ii, 469.
- Chroustchhoff, K. v., artificial production of zircon, ii, 128.
- Church, A. H., turacin, i, 184.
- Ciamician, G., and P. Silber, derivatives of quinol, resorcinol, and phloroglucinol, i, 21.
- leucotin and cotogenin, i, 417.
- pseudopelletierine, i, 287.
- symmetrical dimethoxyquinone, i, 409.
- Ciamician, G., and C. U. Zanetti, basic properties of pyrroline derivatives, i, 602.
- Claisen, L., benzoyl-derivatives of benzoylacetone, i, 577.
- condensation of acetaldehyde with acetone, i, 8.
- hydroxymethylene compounds, i, 360, 480.
- Claisen L., and O. Manasse, action of chlorine on isonitrosoketones, i, 464.
- isonitroso-camphor and its derivatives, i, 479.
- Clark, J., Fleitmann's test with arsenic acid, *TRANS.*, 884.
- improvements in Reinsch's test for arsenic, *TRANS.*, 886.
- the use of sodium peroxide as an analytical reagent, *TRANS.*, 1079.
- Clark, T. H., additive products of benzoquinone and toluquinone, i, 320.
- Clarke, F. W., constitution of pitilolite and mordenite, ii, 77.
- Clarke, F. W., and C. Catlett, platiniferous nickel ore from Canada, ii, 286.
- Clarke, F. W., and E. A. Schneider, constitution of certain micas and chlorites, ii, 78.
- Classen, A., quantitative analysis by electrolysis, ii, 391, 495.
- separation of copper from bismuth, ii, 495.
- Classen, A., and B. Zahorski, action of liquid chlorine on metallic chlorides, ii, 464.
- Claus, A., alkyl and alkylene derivatives of substituted cinchonic acids, i, 728.
- aromatic alkyl ketones, i, 162, 464.
- cinchona alkaloids, i, 181.
- constitution of thiocarbamide and phenyldithiobiuret, i, 341.
- derivatives of quinoline, i, 667.
- isomerism of asymmetrical hydrazones, i, 299.
- oximes, i, 355.
- papaverine ethobromides, i, 489.
- parachlororthotoluidine, i, 699.
- stereochemistry of nitrogen, ii, 157.
- Claus, A., and R. Bayer, monochloro-derivatives of orthoxylene and their relation to the chlororthotoluic acids, i, 586.
- Claus, A., and J. Beckenamp, phenylacridine, i, 718.
- Claus, A., and B. Büttner, alkyl derivatives of 2-phenylcinchonic acid, i, 731.
- Claus, A., and P. Grau, iodoquinolines, i, 669.
- Claus, A., and K. Hoffmann, nitro-derivatives of isoquinoline, i, 366.
- Claus, A., and H. Howitz, 1-bromoquinoline, i, 668.
- hydroxyquinolines, i, 484.
- Claus, A., and O. Massau, 2-nitroquinoline and its derivatives, i, 670.
- Claus, A., and E. Pychlau, 4'-bromonicotinic acid, i, 484.
- Claus, A., and M. Schöller, 1-chloroquinoline, i, 668.
- Claus, A., and E. Stapelberg, parachlororthotoluic acid and its derivatives, i, 580.
- Claus, A., and F. Stohr, alkyl derivatives of quinic acid, i, 728.
- Clement, A. A. See Noyes.
- Clermont. See De Clermont.
- Cleve, P. T. See Carlgren.
- Cochin, D., flame spectra of some metals, ii, 402.
- Cohen, E., and E. Weinschenck, meteoric iron, ii, 20.
- Cohn, G., the condensation products of monobasic acids with resorcinol, i, 719.
- Cohn, G. See also Ehrlich.
- Cohn, R., a complete process of reduction occurring in the animal tissues, ii, 544.
- physiological action of pyridine and naphthalene derivatives, ii, 544.

- Cohn. See Lassar-Cohn.
- Cohnstein, W., alkalinity of the blood during muscular work, ii, 218.
- Colby, G. E., analyses of Californian prunes, apricots, plums, and nectarines, ii, 591.
- Colby, G. E., and H. P. Dyer, analysis of Californian prunes, apricots, and peaches, ii, 140.
- Coleman, J. B., and J. D. Granger, volumetric estimation of calcium phosphate by means of uranium, ii, 301.
- Collie, J. N., the fluorescein of camphoric anhydride, TRANS., 961.
- the production of naphthalene derivatives from dehydracetic acid, TRANS., 329.
- Collie, J. N., and W. S. Myers, the formation of orcinol and other condensation products from dehydracetic acid, TRANS., 122.
- Collier, P., milk of different breeds of cows, ii, 220.
- Colquhoun, W., estimation of urea, ii, 310.
- Colson, A., a limited reaction, ii, 72.
- formula of ordinary tartaric acid, i, 553.
- influence of temperature on the rotatory power of liquids, ii, 255.
- rotatory power of salts of the diamines, ii, 105, 106.
- stereochemistry of malic derivatives: variations in the rotatory power of liquids, i, 457.
- Combes, A., and C. Combes, action of ammonia and of aliphatic amines on acetylacetone, i, 454.
- action of diamines on acetylacetone, i, 454.
- Combes, A., and Le Bel, supposed secondary hexyl alcohol from mannitol, i, 246.
- Combes, A. See also Friedel.
- Coninck. See De Coninck.
- Conrad, M., and W. Fischer, α -naphtholsulphonic acids, i, 221.
- Cooke, Miss E. See Howell.
- Cooke, W. W., and J. L. Hills, abnormal milk, ii, 428.
- Coote, A. H. See Hodgkinson.
- Coppet. See De Koppet.
- Cormimboeuf, H., action of potassium and sodium hydroxides on antimony trioxide, ii, 171.
- crystallised sodium titanates, ii, 125.
- Corse, M. B., and C. Baskerville, glauconite from Hanover Co., Virginia, ii, 287.
- Corselli, G. See Minunni.
- Cossa, A., new series of basic platinum compounds, i, 364.
- Coudon, H. See Müntz.
- Cousin, H., action of sulphuric acid on catechol and on homocatechol, i, 637.
- ethers of homocatechol, i, 258.
- Couturier, F., pinacone and its derivatives, i, 244.
- Cramer, E., volatilization of silica, ii, 164.
- Cremer, M., phloridzin diabetes in frogs, ii, 480.
- physiological action of sugars, ii, 585.
- Cremer, M., and A. Ritter, phloridzin diabetes, ii, 31, 480.
- Cristaldi. See Grassi-Cristaldi.
- Crook, W. G., detection of cotton seed oil in lard, ii, 603.
- Cross, C. F., and E. J. Bevan, explosive nitrates from the jute fibre, i, 295.
- Cross, C. F., E. J. Bevan, and C. Beadle, the interaction of alkali cellulose and carbon bisulphide: cellulose thiosulphocarbonates, TRANS., 837.
- Cross, W., constitution of spherulites in acid eruptive rocks, ii, 287.
- Cross, W., and L. G. Eakins, new occurrence of ptilolite, ii, 77.
- Crossley, A. W. See Schuster.
- Cumenge, E., new mineral from Boléo, Mexico, ii, 417.
- Curci, A., behaviour of xylenes in the organism, ii, 178.
- Curtius, T., azoimide from hydrazine hydrate and nitrous acid, ii, 372.
- hippurylphenylbuzylene: new synthesis of azoimide, i, 463.
- hydrazine derivatives, i, 299.
- Cushny, A. R., alkaloids of *Gelsemium sempervirens*, i, 614.

D.

- Dafert, F. W., estimation of nitrogen in soils, ii, 601.
- D'Aladern, R., heat of formation of some derivatives of indigotin, i, 649.
- Danilewsky, B., physiological action of cocaine, ii, 334.
- Danner, E. W. See Gooch.
- Dashiell, P. J., parethoxyorthotoluenesulphonic acid, i, 343.
- Dashiell, P. J. See also Remsen.
- Da Silva. See Ferreira da Silva.
- Davidson, R. J., chemistry of the tobacco plant, ii, 38.

- De Bell, J. T., cuproplumbite from Butte City, Montana, ii, 286.
 — statuary marble from Rutland, Vermont, ii, 286.
- De Boisbaudran, L., samarium, ii, 323, 526.
- De Bruyn. See Lobry de Bruyn.
- Decey, T., oxalyl derivatives, i, 554.
- De Chalmot, G., pentosans in plants, ii, 430.
 — soluble pentoses in plants, i, 247.
- De Chambrier, P., supposed formation of orthocresol from methyl-salicylic acid, i, 563.
- Decker, H., action of alkalis on pyridine alkyl iodides and similar bases, i, 279.
 — so-called quinolinium bases, i, 365.
 — some ammonium compounds, i, 115.
- De Clermont, P., oxidation of nickel sulphide, ii, 528.
- De Conineck, O., distinction between isomeric amidobenzoic acids and other isomeric compounds of the benzene series, i, 641.
 — isomeric amidobenzoic acids, i, 413, 465.
- De Coppet, L., temperature of maximum density of aqueous solutions, ii, 60.
 — temperature of maximum density of mixtures of alcohol and water, ii, 61.
- Deeley, R. M., a new diagram and periodic table of the elements, TRANS., 852.
- De Forcrand, alkali phenoxides, i, 316.
 — compounds of alkali phenoxides with phenol, i, 409.
 — constitution of phosphoric acid and the thermal value of its three acid functions, ii, 60.
- De Forcrand, R., hydrates of alcohols, i, 291.
- De Hemptinne, A., electrical conductivity of flames and gases, ii, 563.
- Dehérain, P. P., drainage water from arable soil, ii, 338.
 — soil and nitrification, ii, 486.
- De Konineck, L. L., detection of ammonia with Nessler's reagent, ii, 301.
- De Koning, L., estimation of oleic acid, ii, 251.
- Dela Harpe, C. See Reverdin.
- Delisle, A., and A. Schwalm, organic sulphur compounds, i, 35.
- Demarçay, E., simple nature of samarium, ii, 526.
- Demyanoff, N., action of nitrous acid on tetramethylenediamines, i, 453.
- Dengler, L. See Engler.
- Denigès, G., identification and estimation of the lactoses in different milks, ii, 502.
 — metaphosphoric acid as a precipitant of proteids in the estimation of sugar in milk, ii, 248.
 — preparation of sulphites of zinc, magnesium, and cadmium, ii, 277.
- Dennstedt, M., action of propyl alcohol on pyrroline, i, 226.
- De Norwall, F. K. See Einhorn.
- Denoza, M., isoeugenolglycollic acid and eugenolglycollic acid, i, 643.
- Der Heide. See Van Der Heide.
- Deroide, E., estimation of uric acid in urine, ii, 101.
- Der Plaats. See Van der Plaats.
- De Saint Martin, L., elimination of carbonic oxide, ii, 131, 288.
- De Sanderval, dissociation of sodium chloride in presence of heated surfaces of porous clay, ii, 316.
- De Saporta, A., relation between the sp. gr. of acid or saline solutions and the molecular weight of the dissolved substance, ii, 7.
- Desch, C. H. See Burls.
- Dessauer, H. See Buchner.
- Deszàthy, A., solubility of barium and calcium butyrates, i, 547.
- Devarda, A., direct estimation of nitrogen in saltpetre, ii, 343.
- Deventer. See Van Deventer.
- De Visser, L. E. O., experiments with the manocryometer, ii, 563.
 — lecture experiment with the manocryometer, ii, 566.
- Dewar, J. See Liveing.
- Dewèvre, glycogenic function in winter frogs, ii, 218.
- Dianin, A., condensation of ketones with phenols, i, 214.
- Dieck, H. L. See Smith.
- Dieckmann, W. See Bamberger.
- Dierbach, R., anilidosalicylic acid, i, 211.
- Dieterich, E., preparation of cantharidin, i, 600.
- Diller, J. S., mica-peridotite from Kentucky, ii, 79.
 — peculiar lava from Northern California, ii, 578.
- Ditte, A., a cadmium and ammonium chloride battery, ii, 403.
 — decomposition of alkali aluminates by carbonic acid, ii, 279.
 — decomposition of alkali aluminates in presence of alumina, ii, 278.
 — industrial preparation of alumina, ii, 324.
 — Leclanché battery, ii, 355, 402.

- Ditte, A., and R. Metzner, action of antimony on hydrochloric acid, ii, 126.
 ——— action of bismuth on hydrochloric acid, ii, 172.
 Dittmar, W., and J. B. Henderson, gravimetric composition of water, ii, 410.
 Dixon, A. E., action between thiourea and some haloïd derivatives of the fatty acids, TRANS., 815.
 ——— an isomeric form of benzylphenylbenzylthiourea, TRANS., 538.
 ——— desulphurisation of the substituted thioureas, TRANS., 318.
 Dobbie, J. J., and A. Lauder, a new alkaloid from *Corydalis cava*, TRANS., 485.
 Dollfus, W., hydrocinnamaldoxime, i, 710.
 Donath, E., cobalt, ii, 468.
 ——— estimation of aluminium in ferro-aluminium, ii, 96.
 Donnini, P. See Antony.
 Dorp. See Van Dorp.
 Doss, B., pseudobrookite, hæmatite, and anhydrite as sublimation products, ii, 18.
 Doyon, M. See Morat.
 Drechsel, E., behaviour of α -amido-propionic acid at high temperatures, i, 132.
 Dreher, E., and S. v. Kostanecki, constitution of the monhydroxy-xanthenes, i, 1, 217.
 Drehschmidt, H., estimation of cyanogen in gas refuse and in illuminating gas, ii, 50.
 Dreyer, H. See Schmidt.
 Drossbach, G. P., electrolytic estimation of copper, ii, 93.
 Dryfoos, L. A. See Mason.
 Duclaux, absorption of free nitrogen by plants, ii, 138.
 ——— the phosphates of milk, ii, 582.
 Duden, P., pyrazoles from unsaturated acids and hydrazines, i, 231.
 Duden, P. See also Knorr.
 Dudley, C. B., and F. N. Pease, estimation of phosphorus in steel, ii, 553.
 Düll, G. See Linter.
 Duncan, C., and F. Hoppe-Seyler, diffusion of oxygen and nitrogen in water, ii, 62.
 ——— respiration in fishes, ii, 81.
 Dunnington, F. P., and T. C. Whitlock, analysis of "black earth," ii, 293.
 Dunstan, W. R., and F. H. Carr, the aconite alkaloids. Part V. The composition of some commercial specimens of aconitine, TRANS., 491.
 Dunstan, W. R., and F. H. Carr, the aconite alkaloids. Part VI. Conversion of aconitine into isaconitine, TRANS., 991.
 Dunstan, W. R., and T. S. Dymond, the isomerism of the paraffinic ald-oximes, PROC., 1893, 76.
 Dunstan, W. R., and E. F. Harrison, the aconite alkaloids. Part IV. On isaconitine (napelline), TRANS., 443.
 Dunstan, W. R., and H. A. D. Jowett, the aconite alkaloids. Part VII. On some modifications of aconitine aurochloride, TRANS., 994.
 Dunstan, W. R., and W. F. J. Shephard, the identity of caffeine and theïne and the reactions of caffeine with auric chloride, TRANS., 195.
 Dunstan, W. R. See also Cash.
 Dupont, J., preparation of methylbenzoic anilide, i, 268.
 Dupont, J., and H. Jansen, copper oxybromide, analogous to atacamite, ii, 463.
 Dyer, B., and J. F. H. Gilbard, discrimination between genuine and exhausted ginger, ii, 611.
 Dyer, H. P. See Colby.
 Dymond, T. S. See Dunstan.

E.

- Eakins, L. G. See Cross.
 Earle, J. J. See Pickell.
 Earp, Miss A. G., boiling points and melting points of sulphur compounds, ii, 445.
 Easterfield, T. H. See Sell.
 Eaton, R. G. See Howell.
 Ebersbach, F. P., affinity coefficients of aromatic amidosulphonic acids, ii, 450.
 Ebstein, W., physiological action of pentoses, ii, 427.
 Eckel, R. See Töhl.
 Eckenroth, H., and M. Wolf, phenylic and α - and β -naphthyllic salicylates, i, 514.
 Eckstein, F., phenylhydrazodiisobutyronitrile and the products of its hydrolysis, i, 85.
 Edler, manuring potatoes, ii, 593.
 Effront, J., chemical conditions of the action of diastases, i, 187.
 Egoroff, I. V., Reychler's artificial diastase, i, 743.
 ——— wheat diastase, i, 743.
 Ehrenberg, A., ethereal oil from the root of *Aspidium filix mas*, i, 625.
 Ehrlich, P., and G. Cohn, action of acid chlorides on nitrosodimethylaniline, i, 564.

- Eickholz, A., urobilin, i, 538.
 Eijk. See Van Eijk.
 Einhorn, A., dihydrobenzaldehyde, i, 341.
 Einhorn, A., and L. Fischer, dihydroxytropidine, i, 738.
 Einhorn, A., and A. Friedländer, nor-*r*-ecgonine, i, 537.
 Einhorn, A., and A. W. Gilbody, action of chloral on pyridine bases from Messel, i, 527.
 Einhorn, A., and F. K. de Norwall, action of bromine on dihydrobenzaloxime, i, 332.
 — amides of ecgonine, i, 445.
 Einhorn, A., and Y. Tahara, constitution of anhydroecgonine, i, 377.
 Einhorn, A., and R. Willstätter, hydrogenised paratoluic acids, i, 713.
 Eisenlohr, J. See Wolff.
 Elbs, K., derivatives of diphenyltrichlorethane and their conversion into stilbene, i, 271.
 — electrolysis of trichloroacetic acid, i, 250.
 — nitroquinol, i, 640.
 — preparation of ammonium persulphate, ii, 516.
 Ellenberger and Hofmeister, behaviour of sterilised milk towards digestive fluids, ii, 217.
 Ellinger, A. See Marckwald.
 Elroy. See Mac Elroy.
 Elsaesser, E. See Gaess.
 Elten, M. See Seubert.
 Embden, H., alcaptonuria, ii, 82.
 Emery, W. O. See Anschütz.
 Emich, F., behaviour of nitric oxide at a high temperature, ii, 66.
 — microchemical detection of sulphur, ii, 295.
 Emmens, S. H., nickel analysis, ii, 393.
 Engler, C., and L. Dengler, condensation of acetophenone on heating alone or with zinc chloride, i, 512.
 Engler, C., and E. Löw, behaviour of organic acids and ethereal salts at high temperatures, i, 512.
 Engler, C., and L. Singer, recognition of paraffin and of lubricating oil in the distillate of train oil under pressure, i, 493.
 Engler, C., and M. Steude, behaviour of trichloroacetic acid at a high temperature, i, 499.
 Ephraim, J., action of phenylhydrazine on lactones, i, 522.
 — amido-derivatives of quinoline, i, 727.
 — derivatives of kyanidine, i, 735.
 Eppens, A. See Koenigs.
 Erdmann, E., preparation of benzidine, i, 470.
 Erdmann, H., behaviour of sodium and potassium naphthionates at high temperatures, i, 655.
 — dichloronaphthalenes, 651.
 — oxidation of chloroform with chromic acid, and preparation of carbon oxychloride from carbon tetrachloride, i, 681.
 — preparation and nitration of ortho-chlorobenzaldehyde, i, 160.
 — Sandmeyer's reaction and preparation of orthochlorotoluene, i, 150.
 — separation and constitution of isomeric naphthalene derivatives, i, 651.
 — sulphonation of α -naphthylamine, i, 653.
 — synopsis of the naphthylamine-sulphonic acids, i, 655.
 Erdmann, H., and F. Henke, derivatives of 3':1-acetonaphthol, i, 652.
 Erdmann, H., and E. Schwechten, synthetic tri-derivatives of naphthalene, i, 653.
 Erdmann, H., and C. Süvern, compounds of substituted naphthalenesulphonic acids with organic bases, i, 653.
 — isomeric α -mononitronaphthalenemonosulphonic acids, i, 651.
 — perinitronaphthalenesulphonic acid, i, 652.
 Erlenmeyer, E., jun., benzoylamido-cinnamic acid, i, 582.
 — α -benzoylamidophenylpropionic acid, i, 581.
 — condensation of hippuric acid with phthalic anhydride and with benzaldehyde, i, 580.
 — new phenylamidolactic acid from glycocine and benzaldehyde, i, 166.
 — phenylpyruvic and phenylglycidic acids, i, 36.
 — separation of cinnamic acid dibromide into its optically active constituents, i, 582.
 Ernst, O., new tap for vacuum desiccators, ii, 453.
 Ernst, P., hyalin and colloïd, ii, 218.
 — kerato-hyalin, ii, 218.
 Ernst, R., combustion of carbon in air, ii, 461.
 Errera, G., campholamine, i, 108.
 Étard, A., action of zinc chloride on chlorocamphor: relation between camphor and carvacrol, i, 524.
 — aldehydes from terpenes, i, 360.
 — benzoynicotine, i, 736.
 — constitution of nicotine and acetylnicotine, i, 675.
 — melting points of solvents as the inferior limits of solubilities, ii, 111.

- Evans, P., condensation of β -diketones with carbamide and thiocarbamide, i, 129.
 Evans, R. E. See Burls.
 Evans, W. N., obituary notice of, TRANS., 751.
 Ewald, A., influence of heat on gas exchange, ii, 131.
 Ewan, T., absorption spectra of copper salts in aqueous solution, ii, 149.
 Ewell, E. E., carbohydrates of the coffee berry, ii, 84.
 Ewell, E. E., and H. W. Wiley, products of cassava, ii, 430.
 Exner, F., electrochemical investigations, ii, 255.
 Eykman, J. F., formula of tropine, i, 537.
 — refractometric observations, ii, 1.

F.

- Fabris, G. See Villavecchia.
 Fahlberg, C., action of phosphoric chloride on orthobenzoicsulphinide, i, 716.
 Fahrion, W., analysis of oils, ii, 603.
 — Hübl's iodine numbers, ii, 103.
 — new method of fat analysis, ii, 604.
 — testing linseed oil varnish, ii, 56, 148.
 Fairley, T., estimation of chlorine in water, ii, 550.
 Fajans, A., estimation of salicylic acid in presence of phenols, ii, 440.
 Falières. See Barthe.
 Farchy, J. M., and J. Tafel, isomeric diamidosuccinic acids, i, 692.
 Farmakovsky, N., tar from the bark of *Populus tremula*, i, 454.
 Fauvet, C. See Freund.
 Favorsky, A. E., action of potassium carbonate on dichloroketones, i, 391.
 Favrel, G., volumetric estimation of alkalis in alkali arsenites, ii, 598.
 — volumetric estimation of pyrophosphoric acid and alkali pyrophosphates, ii, 597.
 Fayrer, J., cardiac and pulmonary thrombosis, ii, 541.
 Feist, F., formation of coumalin rings, i, 403.
 Fellrath, E. See Beckmann.
 Fenton, H. J. H., the oxidation of tartaric acid in presence of iron, PROC., 1893, 113.
 Féré, C., and L. Herbert, accumulation of potassium bromide in the organism, ii, 176, 217.
 — accumulation of strontium bromide in the organism, ii, 217.
 Fernau, A., isocarbostyryl, i, 417.
 Ferratini, A., conversion of indoles into quinolines, i, 602.
 — tetrahydroisoquinoline, i, 227.
 — trimethyltetrahydroquinoline, i, 227.
 Ferratini, A., and F. Garelli, behaviour of indole and some of its derivatives with respect to Raoult's law, ii, 156.
 Ferratini, A. See also Garelli.
 Ferreira da Silva, S. J., eserine and a new colouring matter derived from it, i, 741.
 Ferrier, C., estimation of sodium sulphide, sulphite, and thiosulphate in glycerol from soap works, ii, 348.
 Fertsch, F. C. See Jacobson.
 Féry, C., study of chemical reactions in a liquid mass by means of the index of refraction, ii, 201.
 Field, Miss E., note on the interactions of alkali haloïds with lead and bismuth haloïds, TRANS., 540.
 Fileti, M., oxidation and derivatives of erucic acid, i, 551.
 — stereoisomeric isopropylphenylglycollic acids, i, 212.
 Fileti, M., and G. Baldracco, homoterephthalic acid, i, 467.
 Fileti, M., and E. Cairola, derivatives of homoterephthalic acid, i, 212.
 Fileti, M., and A. Cantalupo, preparation of zinc ethide, i, 196.
 Finger, H., derivatives of orthamidobenzamide, i, 574.
 Finkbeiner, H. See Liebermann.
 Fiquet, E., condensation of aliphatic aldehydes with cyanacetic acid, i, 455.
 Fireman, P. See Bischler.
 Fischer, B., and B. Grützner, homologues of phenol, i, 563.
 Fischer, E., adonitol, a new pentitol, i, 291.
 — amidoacetaldehyde (ethanalanine), i, 187, 300.
 — formation of isoquinoline, i, 427.
 Fischer, E., and W. L. Jennings, constitution of hydrocyanorosaniline and of magenta, i, 711.
 Fischer, E., and E. Schmidmer, rise of salt solutions in bibulous paper, ii, 109.
 Fischer, L. See Einhorn.
 Fischer, O., orthodiamine derivatives, i, 283.
 Fischer, O., and E. Franck, ammonium derivatives of azines, i, 282.
 Fischer, O., and O. Heiler, oxidation products of orthodiamines, i, 266.

- Fischer, O., and E. Hepp, action of alkalis on paranitrotoluene and on paranitrotoluenesulphonic acid, i, 697.
- constitution of the mauveines, i, 464.
- fluoresceinamide, i, 721.
- naphthyl-red and Magdalar-red, i, 721.
- relation of safranines to indulines, i, 613.
- the induline group, i, 333.
- Fischer, O., and A. Junk, naphthazines, i, 283.
- Fischer, W. See Conrad, Jacobson.
- Fisher, W. W., anhydrous oxalic acid, *PROC.*, 1892, 186.
- Fittig, R., itaconic acids, new isomerides of itaconic, citraconic, and mesaconic acids, i, 691.
- brom-additive products of angelic and tiglic acids, i, 188.
- constitution of the unsaturated acids obtained by boiling unsaturated $\beta\gamma$ -acids with soda, i, 688.
- intramolecular changes in unsaturated acids, i, 189.
- Flavitzky, F., theory of chemical types, ii, 408.
- Fleck, H., alkyl compounds of magnesium, i, 622.
- Flieschhauer, H., condensation of cyanides with ethereal salts by means of sodium ethoxide, i, 396.
- Fleissner, F. See Lippmann.
- Fleurent, E., combination of cuprous cyanide with alkali cyanides, i, 289.
- Flint, E. R., and B. Tollens, estimation of pentosans and pentoses in vegetables, ii, 52.
- oxycellulose and bornesitol, i, 295.
- Foerster, F., compounds of copper acetate with ammonia and with pyridine, i, 131.
- Foerster, O., formation and properties of tetracalcium phosphate, ii, 70.
- valuation of basic slags, ii, 344.
- Forerand. See De Forerand.
- Forster, M. O. See Meldola, Tilden.
- Forte, O., derivatives of cresolglycollic acids, i, 269.
- Fortmann, G., orthomethamidobenzoic acid, i, 414.
- Fortner, P., isoquinoline derivatives, i, 608.
- Foster. See Le Neve Foster.
- Fournier, H., paradiethylbenzene, i, 408.
- pentethylbenzene, i, 409.
- Fox, F., condensation of orthochlorobenzotrichloride by means of metals, i, 351.
- Fränckel, S., glycogen, i, 386.
- Fränkel, E., and F. Reiche, sulphuric acid poisoning, ii, 335.
- Franchimont, A. P. N., pentacetyl derivatives of glucose, i, 246.
- Frank, E. See Fischer.
- Frank, O., absorption of fats, ii, 24.
- Frankel, L. K., detection of lead in urine, ii, 606.
- Frankfurt, S. See Schulze.
- Frankland, P. F., and J. R. Appleyard, salts of glyceric acid, active and inactive: the influence of metals on the specific rotation of active acids, *TRANS.*, 296.
- Frankland, P. F., and J. MacGregor, ethereal salts of diacetyl-glyceric acid in relation to the connection between optical activity and chemical constitution, *TRANS.*, 1419.
- ethereal salts of glyceric acid, inactive and active, *TRANS.*, 511.
- normal butylic, heptylic, and octylic salts of active glyceric acid, *TRANS.*, 1410.
- sarcolactic acid, obtained by the fermentation of inactive lactic acid, *TRANS.*, 1028.
- Freer, P. C., ethylic acetoacetate and ethylic salicylate, i, 66.
- Freer, P. C., and G. O. Higley, reduction of nitric acid by copper, ii, 272.
- Frenkel, M., palladium compounds, ii, 195.
- Frenzel, A., kyllindrite, ii, 576.
- Fresenius, R., separation of barium, strontium, and calcium, ii, 436.
- separation of strontium from calcium, ii, 301.
- Freudenberg, H., electromotive force in electrolytic analyses, ii, 506.
- Freund, M., hydrastine, i, 116.
- Freund, M., and C. Fauvet, geissospermine, i, 446.
- Freund, M., and H. Haase, paranitrophenylmethoxybiazolone and its decomposition products, i, 534.
- Freundler, influence of organic solvents on rotatory power, ii, 562.
- Freundler, P., alkyl tartrates, i, 73.
- Freyer, F., and V. Meyer, ignition temperature of explosive gases, ii, 257.
- Freytag, F. See Kossel.
- Friedel, C., existence of the diamond in the meteoric iron of Cañon Diablo, ii, 174, 288.
- metaldehyde, i, 547.
- reproduction of diamonds, ii, 276.

- Friedel, C., rotatory power of salts of diamines, ii, 105.
 — stereochemical notation, i, 195.
 — stereochemistry, ii, 255.
 — the meteorite from Cañon Diablo, ii, 174, 288.
 Friedel, C., and A. Combes, action of phenylhydrazine on camphoric anhydride and ethereal camphorates, i, 600.
 Friedel, G. See Mallard.
 Friedheim, C., history of the complex inorganic acids, ii, 378.
 — molybdoarsenates, ii, 282.
 — phosphomolybdates, ii, 472.
 — volumetric estimation of free chlorine, ii, 488.
 Friedheim, C., and H. Leo, estimation of acids by calcium carbonate, ii, 342.
 Friedheim, C., and R. Meyer, preparation of tungstates free from molybdenum, ii, 125.
 Friedheim, C., and R. J. Meyer, quantitative separation and estimation of chlorine, bromine, and iodine, ii, 183.
 Friedheim, C. See also Rosenheim.
 Friedländer, A. See Einhorn.
 Friedländer, P., phenolphthaleïn, i, 273.
 Friedlaender, P., and A. Stange, phthaleïnoxime, i, 719.
 Friedmann, A., and L. Gattermann, action of thiocarbimides on aromatic hydrocarbons, i, 153.
 Friedrich, H., lead tetrachloride, ii, 415.
 Fritsch, M. See Buchner.
 Fritsch, P., acetyldiphenylcarbamide, i, 340.
 — chlorination of acetone, i, 303.
 — synthesis of isocoumarin and isoquinoline derivatives, i, 366.
 Fritz, H., relations of the physical and chemical properties of the chemical elements and compounds, ii, 155.
 Fritzsche, E. See Möhlau.
 Fritzweiler, E. See Paal.
 Fromm, E., phenyldithiobiuret, i, 575.
 Fuchs, O. See Zincke.
 Fulton, H. B., specific gravity apparatus, ii, 264.

G.

- Gabriel, S., nutritive value of asparagine, ii, 177.
 Gabriel, S., and W. Michels, triamidopropane, i, 31.
 Gabriel, S., and A. Neumann, conversion of phthalide derivatives into those of *aa*-diketohydrindone, i, 415.
 — — derivatives of phthalazine and isoindole, i, 346.
 — — synthesis of isoquinoline derivatives, i, 228.
 Gabriel, S., and G. Pinkus, amidoketones, i, 734.
 — — phthalazine, i, 732.
 Gärtner, C., pentamethylene and its derivatives, i, 557.
 — — pentamethylenecarboxylic acid, i, 557.
 Gaess, F., and E. Elsaesser, condensation of metaphenylenediamine with α -naphthol, i, 420.
 Gal, J., plastic sulphur from sulphur vapour, ii, 455.
 Gammarelli, P., estimation of nitric acid by means of cinchonamine salts, ii, 297.
 Gantter, F., detection and approximate estimation of cotton seed oil in lard and olive oil, ii, 440.
 — — detection of saccharin in beer, ii, 504.
 — — discrimination of butter from margarin, ii, 603.
 — — iodine absorption, ii, 309.
 — — valuation of hide clippings for glue making, ii, 610.
 Garbutt, L., note on a form of burette for rapid titration, *Proc.*, 1893, 183.
 Garcia, A., ptomaines, i, 538.
 Gardner, J. A. See Marsh.
 Garelli, F., a ketone obtained from ethylic dihydrocollidinedicarboxylate, i, 667.
 Garelli, F., and A. Ferratini, phenanthrene as a solvent in cryoscopic determinations, ii, 512.
 Garelli, F. See also Ferratini.
 Garnier, J., influence of electricity on the carburisation of iron by cementation, ii, 527.
 Garnier, L., separation of arsenic from antimony, ii, 600.
 Garnier, M., toxicological examination for metals, ii, 598.
 Garrett, F. C. See Oliver.
 Garrod, A., urea in the blood of birds, ii, 581.
 Garrod, A. E., urinary hæmatoporphyrin, ii, 480.
 Garros, F., organised ferment from cherry tree gum : pectinose, ii, 180.

- Garzino, L., triphenylpiperazine, i, 428.
- Gascard, A., calculus in muscle, ii, 334.
- myricyl alcohol, i, 683.
- wax of gum lac, i, 548.
- Gassmann, A., hydrogen bromide, ii, 453.
- Gattermann, L., electrolytic reduction of aromatic nitro-compounds, i, 566.
- Gatterman, L. See also Friedmann, Hartmann, Stockhausen, Tust.
- Gaube, J., carbonated albuminuria, ii, 221.
- Gautier, A., a new type of phosphorites, ii, 419.
- formation of natural aluminium and iron phosphates, ii, 536.
- new natural phosphates, ii, 577.
- phosphatic rocks of animal origin and a new type of phosphorites, ii, 419.
- tobacco smoke, i, 226.
- Gautier, H. See Moissan.
- Geelmuyden, H. C., some results of transfusion, ii, 22.
- Geigel, R., and L. Abend, secretion of hydrochloric acid in nervous dyspepsia, ii, 219.
- Genth, F. A., agularite, ii, 214.
- anglesite associated with boleite, ii, 326.
- danalite, ii, 215.
- metacinnabarite, ii, 215.
- penfieldite, a new mineral species, ii, 76.
- Genvesse, P., ethylic carbacetate, i, 306.
- ethylic pyruvate and the product of its condensation by hydrogen chloride, i, 552.
- method of preparing brominated fatty acids, i, 65.
- some substituted benzenoid hydrocarbons, i, 562.
- syntheses with aluminium chloride, i, 505.
- Georgescu, M., benzenesulphonates of the aromatic series, i, 478.
- Gérard, E., ferment in *Penicillium glaucum*, resembling emulsin, i, 774.
- transformation of the albumin of the urine in Bright's disease, ii, 30.
- Gerhard, F., estimation of iron in spring water, ii, 198.
- Gerrard, A. W., estimation of glucose, ii, 248.
- Gerock, J. E. See Schneegans.
- Gfeller, E. See Graebe.
- Ghira, A., atomic refraction of boron, ii, 517.
- cryoscopic behaviour of some acetates of feeble bases, i, 667.
- Gibson, H. B., liberation of nitrogen during putrefaction, ii, 224.
- Gibson, J., on glucinum, TRANS., 909.
- Gigli, T., decomposition of solutions of oxalic acid, i, 395.
- Gilbard, J. F. H. See Dyer.
- Gilbody, A. W. See Einhorn.
- Gill, A. H., condensation of ortho-chlorobenzal chloride by means of metals, i, 351.
- estimation of carbonic anhydride in the air of buildings, ii, 240.
- Gillespie, A. L., bacteria of the stomach, ii, 223.
- Gintl, W. H., urson, i, 601.
- Giorgis, G., estimation of chromium in products of the iron industry, ii, 554.
- Girard, A., migration of the starch of potatoes in the tubers, ii, 485.
- Girard, A. C. See Müntz.
- Giustiniani, E., compounds of malic and fumaric acids with aromatic amines, i, 264.
- Gladky, P., estimation of oxygen in iron, ii, 388.
- Gladstone, J. H., molecular refraction and dispersion, ii, 254.
- reactions of ferric salts with thiocyanates, i, 289.
- Gläser, M., and W. Kalmann, new iodine spring in Austrian Silesia, ii, 579.
- Glaser, C., separation of iron oxide from alumina in phosphatic rocks by fusion with an alkali carbonate, ii, 346.
- Glatzel, E., normal thiophosphates, ii, 458.
- Glazebrook, R. T., and S. Skinner, Clark cell as standard of E.M.F., ii, 107.
- Glinka, F., analysis of silicates by Deville's method, ii, 491.
- Glücksman, C. See Pribram.
- Gmelin, B., constitution of leucine, i, 501.
- Godlewski, E., nitrification, ii, 544.
- Göhlich, W. See Schmidt.
- Görtz, A. See Lellmann.
- Goldschmidt, H., carvole, i, 723.
- Goldschmidt, H., and W. H. van Rietschoten, action of isocyanates on aromatic aldoximes, i, 707.
- isomeric orthonitrobenzaldoximes, i, 709.
- Goldschmiedt, G., laudanine, i, 181.
- Goldschmiedt, G., and F. v. Hemelmayr, scoparin, i, 601.
- Goldschmiedt, G., and F. Schranzhofer, papaverinic acid, i, 180.

- Golenkin, A., and A. Klepikof, oxidation of quinoline by potassium permanganate, i, 44.
- Gomberg, M., trimethylxanthine derivatives, i, 375.
- Gonnard, F., the mesotype group in the Puy-de-Dôme, ii, 287.
- zirconiferous felspathic inclusion in basalt, ii, 418.
- Gooch, F. A., and P. E. Browning, estimation of iodine in haloïd salts by the action of arsenic acid, ii, 488.
- Gooch, F. A., and E. W. Danner, certain points in the interaction of potassium permanganate and sulphuric acid, ii, 15.
- Gooch, F. A., and H. W. Gruener, iodometric estimation of nitrates, ii, 42.
- Gooch, F. A., and J. I. Phinney, estimation of rubidium by the spectro-scope, ii, 240.
- Gore, G., chemical equilibrium in mixed electrolytes, ii, 150.
- method of measuring loss of energy due to chemical union, ii, 63.
- relation of volta-electromotive force to pressure, ii, 256.
- Gossart, E., higher alcohols and other impurities in ethyl alcohol, ii, 393.
- Gourlay, F., proteïds of the spleen and thyroid, ii, 425.
- Gouy, effects of gravity on fluids at the critical point, ii, 112.
- Gow, W. J. See Harris.
- Goyder, G. A., stibiotantalite, a new mineral, TRANS., 1076.
- Graebe, C., bidiphenylenethylene, a red hydrocarbon, i, 38.
- preparation of orthochloro- and orthobromo-benzoic acid, i, 641.
- Graebe, C., and F. Bossel, oxidation of naphthalic acid, i, 593.
- Graebe, C., and E. Gfeller, oxygenated derivatives of acenaphthene, i, 656.
- Graebe, C., and K. Lagodzinski, acridone, i, 649.
- Graebe, C., and A. Philips, hydroxy-derivatives of anthraquinolinequinone, i, 670.
- Graebe, C., and C. A. Wander, phenanthridone, i, 658.
- Graff, W., detection of foreign fats in wool fat, ii, 397.
- Graffenberger, L., estimation of milk fat with Demichel's lactobutyrometer, ii, 55.
- influence of light on metabolic processes, ii, 580.
- Graftian, J. See Petermann.
- Grandis, V., gaseous tension in the blood and serum of peptonised animals, ii, 131.
- Grandmougin, E. See Michel, Noelting, Witt.
- Grandval, A., and H. Lajoux, estimation of alkaloids, ii, 608.
- estimation of caffeine, ii, 559.
- Grandval, A. See also Lajoux.
- Granger, A., cuprous phosphide, ii, 526.
- Granger, J. D. See Coleman.
- Grassi-Cristaldi, G., action of hydrochloric acid on the santonones: bisdihydrosantoninic acid, i, 425.
- fumaroid and maleinoid structure of some of the derivatives of the santonins, i, 425.
- oxidation products of the santonic acids, diparaxylyl and diphenyl, i, 665.
- reduction products of santonins: santone and isosantonone, i, 110.
- Grau, P. See Claus.
- Gray, A. D. See Hooker.
- Green, A. G., qualitative analysis of coal-tar colouring matters, ii, 610.
- the oxidation of paratoluidine, TRANS., 1395.
- Green, J. R. See Vines.
- Greene, W. H., and W. H. Wahl, method for reducing metallic oxides, ii, 520.
- Gregor. See Mac Gregor.
- Gréhan, N., and E. Martin, physiological action of opium smoke, ii, 179.
- Griessmayer, V., dextrin, i, 684.
- Griffiths, A. B., γ -achroglobin, a new respiratory globulin, i, 236.
- δ -achroglobin from the blood of certain mollusca, i, 615.
- echinochrome, a respiratory pigment, i, 59.
- new bacillus in rain water, ii, 83.
- pigments of lepidoptera, i, 236.
- ptomaine from the urine in cases of eczema, i, 614.
- ptomaines from the urine in erysipelas and puerperal fever, i, 183.
- respiratory globulin from the blood of *Chiton*, i, 60.
- Griggi, G., detection of hydrogen peroxide, ii, 233.
- Grigorovitch, A., and D. Pavloff, action of acid chlorides on zinc ethide, i, 124.
- Grimaldi, G. P., Cailletet and Colardeau's method of determining critical points, ii, 111.
- Grimaux, E., quinine double salts, i, 115.
- Grimaux, E., and J. V. Laborde, physiological action of cupreine and its derivatives, ii, 223.
- Grimm, F., urobilin, ii, 429.

Grindley, H. S., and C. L. Jackson, derivatives of chloranil, i, 322.
 Grindley, H. S. See also Jackson.
 Griner, G., some cases of isomerism in the C_6 series, i, 237.
 — synthesis of erythritol, i, 450.
 Grittner, A., estimation of sulphur in coal, ii, 89.
 — qualitative separation of the barium group, ii, 92.
 Grossmann, J., estimation of nitrites, ii, 87.
 Grossmann, O. v., oxidation products of behenolic acid, i, 305.
 Groves, E. W., chemical stimulation of nerves, ii, 221.
 Gruener, H., iodometric estimation of nitrates, ii, 550.
 — stability of standard solutions of tartar emetic, ii, 600.
 Gruener, H. W. See Gooch.
 Grützner, B. See Fischer, Poleck.
 Guareschi, I., synthesis of hydro-pyridine compounds, i, 484.
 Gucci, P., action of caustic alkalis on phthalide, i, 644.
 — derivatives of phenylenediamine, i, 638.
 Gucci, P. See also Cannizzaro.
 Günther, H. See Zincke.
 Guérin, G., and H. Thorion, ammonium magnesium urate, ii, 99.
 Guglielmo, G., vapour tensions of solutions of sulphur and phosphorus in carbon bisulphide, ii, 511.
 Guichard, estimation of starch, ii, 249.
 — polarimetric examination of gums, ii, 502.
 Guillot, rapid estimation of caffeine in tea and coffee, ii, 608.
 Guinard, L., resistance of goats to the action of morphine, ii, 335.
 Guntz, probable presence of iron carbonyl in coal gas, ii, 73.
 Gustavson, G., action of stannic chloride on halogen derivatives of methane, i, 121.
 Guye, P. A., determination of the molecular weight at the critical point, ii, 204.
 — malic acid derivatives, i, 500.
 — molecular dissymmetry, ii, 204.
 — product of asymmetry, ii, 561.
 — rotatory power of a substance belonging to an homologous series, ii, 561.
 Guye, P. A., and L. Chavanne, rotatory power of ethereal salts of valeric and glyceric series, ii, 561.
 Guyot, A. See Haller.
 Györy, S., volumetric estimation of arsenic and antimony, ii, 554.

H.

Haase, E., melting point determinations, ii, 357.
 Haase, H. See Freund.
 Haefcke, H., chemical constitution of hornblende, ii, 130.
 Haegeler, E., condensation products of amidophenols, i, 273.
 Häussermann, C., preparation of α -trinitrotoluene, i, 14.
 — sodium perchromate, ii, 471.
 Hagemann, C. T. L., action of methylenic iodide on ethylic acetoacetate, i, 393.
 — new extraction apparatus, ii, 567.
 Hahn, O. See Lippmann.
 Haig, A., physiological action of uric acid ii, 585.
 Haldane, J., and J. L. Smith, toxic action of expired air, ii, 223.
 Hall, J. A., the nitro-derivatives of phenolphthaleïn, *Proc.*, 1893, 14.
 Haller, A., function of camphoric acid, i, 361.
 Haller, A., and E. Brancovici, alkyl benzeneazocyanacetates, i, 465.
 Haller, A., and A. Guyot, derivatives of phenolphthaleïn and fluoresceïn, i, 419.
 — diazoamidobenzene and para-diazotoluene benzoates, i, 331.
 Halliburton, W. D., proteïds of kidney and liver cells, ii, 133.
 — proteïds of nervous tissue, ii, 478.
 Halliburton, W. D., and T. G. Brodie, intravascular coagulation, ii, 541.
 Hallopeau, L. A., estimation of peptone by precipitation as mercury peptonate, ii, 104.
 Hamburger, A., astochite and dahllite, ii, 421.
 Hamburger, H. J., action of physiological saline solution on blood corpuscles, ii, 426.
 — influence of acids and alkalis on defibrinated blood, ii, 332.
 — influence of acids and alkalis on the determination of the osmotic pressure in relation to the red blood corpuscles, ii, 175.
 Hampe, W., simultaneous precipitation of copper and antimony by the electric current, ii, 72.
 Handy, J. O., rapid estimation of phosphorus in iron, steel, and ores, ii, 44.
 Hannay, J. B., analysis of pigments ground in oil, ii, 494.
 — metallurgy of lead, ii, 464.
 Hannay, J. B., and A. E. Leighton, the supposed saponification of linseed

- oil by Dutch white lead, *PROC.*, 1893, 122.
- Hanriot and C. Richet, chloralose, a derivative of chloral, and its physiological properties, i, 247.
- Hantzsch, A., compounds containing a double linking between nitrogen and carbon, i, 409.
- hydrochlorides of stereoisomeric aldoximes, i, 411.
- stereochemistry of unsymmetrical hydrazones, i, 207.
- thiocyanacetone, i, 64.
- Hantzsch, A., and A. Miolati, anhydri-
sation of oximido-acids, i, 574.
- — formation of inner anhydrides from ketoximic acids, i, 583.
- Hantzsch, A., and A. Werner, stereoisomerism of the benzhydroxamic acids, i, 710.
- Hardin, M. B., available phosphoric acid and the soluble potash in cotton seed meal, ii, 594.
- Harland, R. H., analysis of ground white lead, ii, 494.
- Harley, V., diabetic coma, ii, 543.
- obstructive jaundice, ii, 30.
- pancreatic diabetes, ii, 31.
- physiological action of sugar, ii, 584.
- Harnack, E., and J. Remertz, influence of chloral hydrate and amylene hydrate on metabolism, ii, 543.
- Harpe. See De la Harpe.
- Harries, C. D., action of ethylenic bromide on phenylhydrazine, i, 571.
- Harris, V. D., and W. J. Gow, pancreatic juice in different animals, ii, 22.
- Harrison, E. F. See Dunstan.
- Hartley, W. N., method of observing the spectra of easily volatile metals and their salts, and of separating their spectra from those of the alkaline earths, *TRANS.*, 138.
- observations on the origin of colour and on fluorescence, *TRANS.*, 243.
- physical character of the lines of the spark spectra of the elements, ii, 2.
- Hartley, W. N., and H. Ramage, manganese borate, its constitution and properties, *TRANS.*, 129.
- Hartmann, A. See Liebermann.
- Hartmann, C., and L. Gattermann, hydrolysis of phenolic ethers and of ethereal salts by means of aluminium chloride, i, 152.
- Hartmann, C., and V. Meyer, iodoxybenzoic and iodosobenzoic acids, i, 577.
- Hartmann, G., derivatives of d-mannoheptonic acid, i, 148.
- Hartog, P. J., and W. E. Sims, thionyl bromide, *PROC.*, 1893, 10.
- Haselhoff, manufacture and composition of linseed cake and meal, ii, 38.
- Hassreidter, V. See Prost.
- Hausdörfer, A. See Bischoff.
- Hausser, J., cryoscopic studies in the benzene series, i, 270.
- Hausser, J., and P. T. Muller, decomposition of diazo-compounds, i, 81.
- Hawkins, E. M. See Meldola.
- Haworth, E., and H. W. Perkin, jun., synthesis of pentamethylenecarboxylic acid, hexamethylenecarboxylic acid, and azelaic acid, i, 694.
- Headden, W. P., alloys of iron and tin, ii, 211.
- kehoeite, a new phosphate from S. Dakota, ii, 537.
- stannite from the Black Hills, Dakota, ii, 325.
- tungstous oxide associated with columbous oxide, ii, 531.
- Hebebrand, A., changes in mouldy bread, ii, 545.
- Heberdey, P. P., crystallised slags from Raibl, ii, 129.
- Hébert, A., fermentation of manure, ii, 182.
- Heerlein, W., influence of caffeine and coffee distillate on metabolism, ii, 329.
- Hegner, O., estimation of oleic acid, ii, 251.
- Heide. See Vander Heide.
- Heiler, O. See Fischer.
- Helbing, H., and F. W. Passmore, detection of foreign fat in wool fat, ii, 351.
- Held, A., condensation of alkyl acetylcyanacetates, i, 456.
- Helff, A., sulphides of phosphorus, ii, 569.
- Helme, T. A., foetal urine, ii, 428.
- Helmolt, H. v., double fluorides, ii, 373.
- Hemmelmayr, F. v., meconinemethyl phenyl ketone, i, 181.
- Hemmelmayr, F. v. See also Goldschmiedt.
- Hempel, W., estimation of sulphur in coals and organic substances, ii, 187.
- use of sodium peroxide in analysis, ii, 387.
- Hempel. See Alberti.
- Hemptinne. See De Hemptinne.
- Henderson, J. B. See Dittmar.
- Hendrixson, W. S. See Hill.
- Henke, F. See Erdmann.
- Henrich, F. See Jacobson.

- Henriques, R., analysis of rubber goods, ii, 399.
 — derivatives of 1:4-amidonaphthalene, i, 39.
 — estimation of copper by Volhard's thiocyanate method, ii, 345.
- Henry, C., phosphorescent zinc sulphide, ii, 72.
 — phosphorescent zinc sulphide as a photometric standard, ii, 202.
- Henry, P., and H. v. Pechmann, action of nitrous acid on ethylic acetonedicarboxylate, i, 397.
- Hentzschel, W., adipin ketone from wood oil, i, 556.
- Hentzschel, W., and J. Wislicenus, adipin ketone, i, 555.
 — pentamethylenic alcohol and its derivatives, i, 556.
- Hepp, E. See Fischer.
- Herbert, L. See Féré.
- Hermens, R. See Michaelis.
- Herroun, E. F., electromotive forces of gold and of platinum cells, ii, 149.
- Herschmann, P., action of sulphuric acid on the pinacone of methyl ethyl ketone, i, 547.
- Herty, C. H., mixed double haloïds of lead and potassium, ii, 278, 465.
- Herz, F. J., amyloid, a component of milk and dairy products, i, 447.
- Herzberg, W., detection of resin in the sizing of paper, ii, 148.
- Herzfelder, A. D., substitution in the fatty series, i, 449.
- Herzig, J., methylbrazilin, i, 426.
- Herzig, J., and T. v. Smoluchowski, quercetin derivatives, i, 413.
- Hess, W., analysis of bone-meal, fish guano, and similar phosphates, and nitrogenous manures, ii, 389.
- Hesse, O., carotene, ii, 33.
 — cinchonine, i, 677.
 — coca leaves, i, 57.
 — flowers of *Tagetes glandulifera*, i, 623.
 — hydrocoton and its derivatives, i, 718.
 — hyoscyne and oscine, i, 679.
 — melting point of cocaine hydrochloride, i, 738.
 — quinine, cinchonidine, and cinchonine, i, 676.
- Heumann, K., and C. Bachofen, behaviour of indigo when heated with alkalis, i, 270.
- Heusler, F. See Lorenz.
- Heut, G., conine and nicotine, ii, 607.
- Hewitt, J. T., chlorinated phenylhydrazines. Part II, TRANS., 868.
 — citraconfluoresceïn. Part II, TRANS., 677.
- Hewlett, R. T., fractional heat coagulation of proteïds, i, 59.
 — lactoglobulin, ii, 134.
- Higley, G. O. See Freer.
- Hildebrandt, H., hydrolytic ferments, ii, 329.
 — nutritive value of albumoses, ii, 539.
- Hilgard, E. W., estimation of potassium, ii, 300.
 — formation of alkali carbonates in nature, ii, 165.
- Hill, H. B., and W. S. Hendrixson, chlorosulphopyromucic acids, i, 313.
- Hill, H. B., and W. L. Jennings, methylfurfuraldehyde and methylpyromucic acid, i, 311.
- Hill, R. T., hæmatite and martite iron ores in Mexico, ii, 325.
- Hillebrand, W. F., further example of the isomorphism of thorium and uranium dioxides, ii, 378.
 — preparation and sp. gr. of uranium dioxides, ii, 378.
 — zinc-bearing spring waters from Missouri, ii, 81.
- Hiller-Bombien, O., geoffroya barks, i, 182.
- Hills, J. L. See Cooke.
- Hiltner, L. See Nobbe.
- Hinman, B. C., volumetric estimation of zinc, ii, 303.
- Hinrichs, G., critical examination of the fundamental determinations of Stas on potassium chlorate, ii, 163.
 — determination of the atomic weight by the method of limit, ii, 316.
 — general method for the calculation of the atomic weight from the data of a chemical analysis, ii, 317.
 — mechanical comparison between the cyanogen radicle and the halo-gens, i, 1.
 — specific heat of the atoms and their mechanical constitution, ii, 59.
 — Stas's determinations of the atomic weight of lead, ii, 277.
- Hinsberg, O., benzenesulphonamides, i, 168.
- Hirsch, R., β -hydroxynaphthoic acid (m. p. 216°), i, 476.
- Hirschfeld, F., proteïd in diet, ii, 540.
- Hirschsohn, E., detection of cineole in ethereal oils, ii, 395.
 — occurrence of bornylic acetate in the ethereal oils of *Abies sibirica* and *Abies pectinata*, i, 224.
- Hittorf, W., electromotive force of galvanic combinations, ii, 150.
- Hjelt, E., anhydride formation in the case of substituted succinic acids, i, 693.

- Hjelt, E., relative velocity of lactone formation in the case of bibasic γ -hydroxy-acids, i, 71.
- Hobbs, W. H., rose-coloured lime and alumina-bearing tale, ii, 538.
- Hodgkinson, W. R., a magnesium compound of diphenyl, *Proc.*, 1893, 80.
- Hodgkinson, W. R., and A. H. Coote, action of phenylhydrazine on mono- and di-carboxylic acids at elevated temperatures, *Proc.*, 1892, 219.
- Hodgkinson, W. R., and L. Limpach, on some new bases. Part II. Methoxyamidodimethylbenzene (1:2:4:6) and its derivatives, *Trans.*, 104.
- some relations between constitution and physical constants in the case of benzenoid amines, *Proc.*, 1893, 41.
- Hodgkinson, W. R., and C. C. Trench, action of ammonia on sulphates, ii, 118.
- Hodgkinson, W. R., and J. Young, action of sulphurous anhydride on oxy-salts, ii, 115.
- Höland, R., estimation of sulphur in organic liquids, ii, 433.
- Hönig, M., and G. Spitz, analysis of mixtures of saponifiable and unsaponifiable fats, ii, 102.
- Hoerlin, J. See Koenigs.
- Hoff, J. See Weidel.
- Hoffmann, K. See Claus.
- Hofmann, K., colouring matters of the triphenylmethane series, i, 472.
- Hofmann, K., and G. Krüss, action of charcoal on solutions of the salts of the rare earths, ii, 374.
- holmium oxide, ii, 466.
- terbia, ii, 466.
- Hofmann, K. B., specific gravity of titanium, ii, 379.
- Hofmeister. See Ellenberger.
- Hogg, T. W., analysis of ferrosilicon and siliceous spiegel, ii, 304.
- Hohmann, C. See Nernst.
- Hollemann, A. F., action of amines and ammonia on the dinitrosaclys, i, 205.
- estimation of calcium in basic slag, ii, 241.
- estimation of potassium by the Lindo-Gladding process, ii, 344.
- solubility of insoluble salts, ii, 519.
- structure of fulminates: dibromonitracetonitrile, i, 494.
- volumetric estimation of phosphoric acid, ii, 490.
- Holm, J. C. See Jörgensen.
- Holt, A., and J. Baruch, action of sulphuric acid on behenic acid, i, 393.
- Hoogewerff, S., and W. A. Van Dorp, ethylic hydrogen camphorate, i, 599.
- orthocyanobenzoic acid, i, 268.
- substituted iso-imides of camphoric acid, i, 599.
- Hooker, S. C., the constitution of lapachol and its derivatives. Part II. The azines of the lapachol group, *Trans.*, 1376.
- the conversion of para- into ortho-quinone derivatives, *Proc.*, 1893, 13.
- Hooker, S. C., and A. D. Gray, dibromo- β -lapachone, its preparation and reactions, *Trans.*, 434.
- Hopkins, C. G. See Orndorff.
- Hopkins, F. G., estimation of uric acid, ii, 395.
- Hoppe, E. See Weidel.
- Hoppe-Seyler, F. See Duncan.
- Horbaczewski, J. See Kossel.
- Hosaeus, H., action of β -naphthol on formaldehyde, i, 100.
- β -hydroxynaphthoic acid, i, 355.
- lactone from formaldehyde and pyruvic acid, i, 628.
- pentaglycerol, i, 617.
- Hote. See L'Hote.
- Hotter, E. See Nobbe.
- Howell, E. E., Mt. Joy meteorite, ii, 216.
- Howell, F. J. See Bischler.
- Howell, W. H., Miss E. Cooke, and R. G. Eaton, action of inorganic salts on the heart, ii, 221.
- Howitz, H. See Claus.
- Huber, A. See Arthus.
- Hüfner, G., dissociation of oxyhæmoglobin in aqueous solution, i, 616.
- Hughes, R. E., properties of dry hydrogen sulphide, ii, 164.
- water as a catalyst, ii, 462.
- Hughes, R. E., and F. R. L. Wilson, action of dried hydrogen chloride on Iceland spar, ii, 208.
- Hugouenq, L., filtration of casein solutions through porcelain, i, 540.
- Hummel, J. J. See Perkin.
- Hundeshagen, F., Eschka's process for the estimation of sulphur, ii, 239.
- Huppert, glycogen in blood and pus, ii, 541.
- occurrence of glycogen in blood, ii, 176.
- specific rotatory power of glycogen, i, 619.
- Hussak, E., brazilite, ii, 286.
- zeolites from Brazil, ii, 422.

- Hutchins, C. C., absorption of radiant heat by alum, ii, 5.
 Hutchinson, A., and W. Pollard, note on lead tetracetate, TRANS., 1136.

I.

- Igelström, L. J., chondrostibian, a new Swedish mineral, ii, 577.
 — friedelite from the Sjö mine, Sweden, ii, 130.
 — melanostibian, a new Swedish mineral, ii, 382.
 Ikuta, M., metamidophenol and its derivatives, i, 265.
 Inoko, Y., hæmoglobin which contains phosphorus, i, 616.
 Irisawa, T., lactic acid in blood and urine, ii, 136.
 Iritzer, S. See Strache.

J.

- Jackson, C. L., and H. S. Grindley, hemiacetals derived from substituted chloranils, i, 563.
 Jackson, C. L. See also Grindley.
 Jacobi, F., and C. Stoehr, a homologue of coniine, i, 442.
 Jacobi, H., birotation and hydrazone formation of some sugars, i, 125.
 Jacobi, W. See Michaelis.
 Jacobson, P., reduction products of azo-compounds, i, 327.
 Jacobson, P., F. C. Fertsch, and W. Fischer, reduction products of azo-compounds, i, 327.
 Jacobson, P., F. Henrich, and J. Klein, reduction products of azo-compounds, i, 327.
 Jäger, W., purification of mercury, ii, 322.
 Jaffé, B., laboratory apparatus for distillations in superheated steam, ii, 163.
 Jaffé, M., dibenzamide and tribenzamide, i, 29.
 Jahn, H., heat of vaporisation of organic compounds, ii, 445.
 Jahn, H. See also Landolt.
 Jahns, E., occurrence of betaine and choline in wormseed (*Artemisia gallica*), ii, 485.
 Jannasch, P., separation of lead from silver in ammoniacal solution by means of chromic acid, ii, 493.
 — separation of metals in alkaline solution by hydrogen peroxide, ii, 492.

- Jannasch, P., and K. Aschoff, direct quantitative separation of chlorine and iodine, ii, 183.
 — — — new direct separation of chlorine, bromine, and iodine, ii, 295.
 — — — separation of iodine, bromine, and chlorine. Estimation of bromine in mineral waters and mother liquors, ii, 595.
 Jannasch, P., and J. Mai, quantitative separations in presence of hydroxylamine, ii, 500.
 Jannasch, P., and W. Remmler, quantitative separation of the metals of the hydrogen sulphide group by means of bromine vapour, ii, 437.
 Jansen, H. See Dupont.
 Japp, F. R., and F. Klingemann, reduction of α -diketones, TRANS., 770.
 Japp, F. R., and T. S. Murray, synthesis of oxazoles from benzoin and nitriles, TRANS., 469.
 Jaubert, G. F., 1:1'-naphthalic acid and its derivatives, i, 477.
 Jaumann, G., attempt to found a chemical theory on a basis of physical comparison, ii, 10.
 Jean, F., analysis of impure galena: estimation of copper and zinc, ii, 493.
 — estimation of manganese in minerals and in alloys, ii, 498.
 — volumetric estimation of copper, iron, antimony, and zinc in zinc powder, ii, 492.
 Jean, F., and Trillat, estimation of potassium, ii, 46.
 Jedlicka, K., action of ethylenediamine on nitrophenols and the corresponding halogen derivatives, i, 699.
 — derivatives of paratertiarybutylphenol, i, 636.
 Jennings, W. L. See Fisher, Hill.
 Jensen, A. See Wislicenus.
 Jenty, S., influence of vegetation on the pressure of carbonic anhydride in the air of soils, ii, 341.
 Jesurin, J. A., action of phosphorus pentachloride on orthobenzoic-sulphinide, i, 715.
 Joannis, A., action of carbonic oxide on sodammonium and on potassammonium, ii, 520.
 — action of oxygen on sodammonium and potassammonium, ii, 462.
 — fusion of calcium carbonate, ii, 117, 167.
 — molecular weights of sodammonium and potassammonium, ii, 115.
 Jörgensen, A., and J. C. Holm, Effront's method for the purification

- and preservation of yeast by means of hydrofluoric acid, ii, 481.
- Johnson, E. S. See Witt.
- Johnson, G. S., organic bases in the juice of flesh, i, 55.
- source of error in the ultimate analysis of organic substances, ii, 306.
- Johnson, S. W., analyses of tobacco stalks when cut and after curing, ii, 592.
- chemical changes in tobacco during fermentation, ii, 592.
- Johnston, W. R. See Wells.
- Jolles, A. F., estimation of phosphoric acid in basic slag, ii, 88.
- Joly, A., ammoniacal derivatives of ruthenium chloride, ii, 172.
- physical properties of fused ruthenium, ii, 285.
- Joly, A., and E. Leidié, atomic weight of palladium, ii, 284.
- Joly, A., and M. Vézes, osmium, ii, 324.
- Jones, A., electrical calamine from Wythe Co., Virginia, ii, 286.
- Jones, E. L., chlorosis, ii, 541.
- Jones, H. C., freezing points of very dilute solutions, ii, 263, 366, 447.
- the freezing points of dilute solutions of sodium chloride, ii, 447.
- Jones, L. M. See Thorpe.
- Jowett, H. A. D. See Dunstan.
- Jüptner, H. v., estimation of aluminium in ferroaluminium, ii, 391.
- Jürgens, B. H. See Van Deventer.
- Juillard, P., indigotintrisulphonic and indigotintetrasulphonic acids, i, 348.
- Turkey-red oil, i, 455.
- Jukovsky, M., oxidation of brassidic acid, i, 550.
- Jukovsky, S., octonaphthylene and octonaphthenic alcohol, i, 420.
- Jumeau, P. L., estimation of ammonium thiocyanate in nitrogenous manures, ii, 347.
- estimation of thiocyanic, hydrocyanic, and hydrochloric acids, ii, 503.
- Jungfleisch, E., and E. Leger, cinchonibine, i, 679.
- Junghahn, A., and A. Reissert, action of paratoluidine on dibromosuccinic acid. New derivatives of dianilidosuccinic acid, i, 565.
- Junk, A. See Fischer.

K.

- Kablukoff, I., avidity of acids in aqueo-alcoholic solutions, ii, 157.
- conductivity of electrolytes in various solvents, ii, 151.
- vapour pressures of aqueo-alcoholic solutions of salts, ii, 154.
- Kablukoff, I., and A. Tsakoni (Zaccani), rate of sugar inversion in aqueo-alcoholic solutions, ii, 160.
- Kablukoff, I. See Louguinine.
- Kahler, M., new drying oven, ii, 162.
- Kalb, G. See Pfeiffer.
- Kalecsinszky, A. v., continuous gas evolution apparatus, ii, 65.
- Kalmann, W. See Gläser.
- Kanonnikoff, I. I., rotatory power of sugars, i, 186.
- Karplus, J. P., production of hydrogen sulphide and methyl mercaptan by a bacterium, ii, 335.
- Karslake, W. J., volumetric estimation of cobalt, ii, 194.
- Karsten, W., condensation of cinnamic acid with hydrocarbons, i, 513.
- Kastle, J. H., decomposition of silver chloracetate, ii, 266.
- Kastle, J. H., and B. C. Keiser, decomposition of chloracetates and bromacetates, i, 624.
- Kauffmann, H. See Auwers.
- Kayser, H., and C. Runge, spectra of aluminium, indium, and thallium, ii, 313.
- ultra-red spectra of the alkalis, ii, 313.
- Kebler, L. F., detection of chlorine, bromine, and iodine, ii, 343.
- Kehrer, E. A., and W. Kleberg, β -furfurallevulinic acid: a new synthesis of coumarone derivatives, i, 254.
- Kehrmann, F., complex inorganic acids, ii, 282, 378, 574.
- phospholuteogunstic acid, ii, 472.
- Kehrmann, F., and J. Messinger, alkyl orthodiamines, i, 199.
- oxidation products of alkyl derivatives of orthodiamines, i, 324.
- Kehrmann, F., and N. Pickersgill, some new complex oxalates, i, 552.
- Keiser, B. C. See Kastle.
- Keller, C. C., estimation of emetine in ipecacuanha root and its fluid extract, ii, 397.
- Keller, H. F., and E. F. Smith, atomic weight of palladium, ii, 73.
- Kemp, J. F., basic dyke thought to contain leucite, ii, 539.
- Kempinski, S., condensation of

- chlorobenzile with phenol and with mono- and di-methylaniline, i, 354.
- Kenngott, A., composition of helvine, ii, 422.
- formula of tourmaline, ii, 422.
- Kerkhoff, F. See Wallach.
- Kerp, W., action of ammonia on mesiten lactone and its derivatives, i, 554.
- Kessler, A., action of iodine on sodium propoxide, i, 383, 682.
- Keussler, E. v., estimation of nitrogen in nitrocellulose, ii, 184.
- Kijner, N., action of sodium on epichlorhydrin, i, 383.
- hydrogenisation of benzene, i, 150, 460.
- Kiliani, H., derivatives of digitogenin, i, 665.
- preparation of pure digitenin, i, 665.
- Kiliani, H., and H. Sanda, decomposition of galactose by calcium hydroxide, i, 546.
- Killgren, A. G., and L. F. Nilson, Swedish fodder plants, ii, 592.
- Kinch, E., *Lathyrus sylvestris*, ii, 547.
- Kinnear, J. B., estimation of solids and fat in milk, ii, 559.
- Kipping, F. S., a new synthesis of hydrindone, *PROC.*, 1892, 216.
- action of phosphoric anhydride on fatty acids, *TRANS.*, 452.
- formation of the ketone 2:6-dimethyl-1-ketohexaphane from dimethylpimelic acid, *PROC.*, 1893, 68.
- melting points of compounds of similar constitution, *TRANS.*, 465.
- the reduction products of dimethyldiacetylpentane, *TRANS.*, 111.
- Kipping, F. S., and W. J. Pope, genesis of new derivatives of camphor containing halogens by the action of heat on sulphonic chlorides, *PROC.*, 1893, 130.
- — studies of the terpenes and allied compounds. The sulphonic derivatives of camphor, *TRANS.*, 548.
- Kipping, F. S. See also Armstrong.
- Kirchsen, T. See Wislicenus.
- Kistyakovsky, V., preparation of glycogen from the liver and muscles, i, 618.
- velocity of etherification, ii, 9.
- Klages, A., and E. Knoevenagel, formation of stilbene, i, 350.
- Klaudy, J., behaviour of aluminium towards mercuric salts, ii, 376.
- Kleberg, W. See Kehrer.
- Klebs, E., diamidopropionic acid, i, 686.
- Kleeberg, A., detection of wheat flour in rye flour, ii, 250.
- Klein, feeding experiments with sunflower cake on cows, ii, 328.
- Klein, J., action of phosphoric chloride on santonin, i, 425.
- derivatives of santonin, i, 425.
- santonin, i, 111, 112, 664.
- santoninoxime and santoninoximic acids, i, 363.
- Klein, J. See also Jacobson.
- Klepikoff, A. See Golenkin.
- Klimont, J., detection and estimation of neutral fats in mineral oil, ii, 604.
- Klingemann, F., condensation of benzaldehyde with deoxybenzoïn, i, 353.
- condensation of deoxybenzoïn with aldehydes and ketones, i, 589.
- diphenylacetic acid, i, 590.
- method for the simultaneous estimation of carbon and nitrogen in organic compounds, ii, 501.
- new nitrogenous organic acid, i, 602.
- note on acetanhydrocitric acid, *TRANS.*, 699.
- transmission of alcohol to milk, ii, 219.
- Klingemann, F. See also Japp.
- Klinger, A., and A. Bujard, estimation of citric acid in wine, ii, 54.
- Klobb, T., action of heat on zinc permanganate, ii, 467.
- isomorphism amongst anhydrous alums, ii, 572.
- Klobbie, E. A. See Van Bemelen.
- Kloepfel, E., iodoxy- and iodoso-derivatives of paratoluic acid, i, 581.
- Klug, F., and V. Olasavsky, effect of work on the excretion of phosphoric acid, ii, 583.
- Knight, F. C., volumetric estimation of lead, ii, 302.
- Knoevenagel, E., formation of cycloïd compounds from 1:5-diketones: structural isomeride of camphor, i, 419.
- synthesis of phenols from ethylic acetoacetate, i, 697.
- Knoevenagel, E., and R. Weissgerber, benzylidenedeoxybenzoïn, i, 353.
- stereoisomeric benzamarones, i, 352.
- Knoevenagel, E. See Klages.
- Knorr, L., the pyrazoline reaction, i, 229.
- Knorr, L., and P. Duden, isomerism of the diphenylpyrazoles and of the pyrazole derivatives from ethyl benzoylacetate and ethyl benzalacetate, i, 230.

- Knorr, L., and P. Duden, pyrazole derivatives of unsaturated acids and hydrazines, i, 229.
- Knorre, G. v., separation and estimation of pyrophosphoric and metaphosphoric acids, ii, 299.
- separation of nickel and cobalt by means of nitroso- β -naphthol, ii, 500.
- Knudsen, P., action of bromine on aldehydecollidine, i, 43.
- Kobert, R., saponins, i, 424.
- König, A., α -hydrindone and its derivatives, i, 586.
- Koenig, G. See Schmidt.
- Koenigs, W., oxidation products of apocinchene, i, 376.
- Koenigs, W., and A. Eppens, camphorone, i, 361.
- Koenigs, W., and J. Hoerlin, sulphocamphylic acid, i, 363.
- Koenigs, W., and E. Wagstaffe, condensation of chloral and butylchloral with acetone and acetophenone, i, 302.
- Köster, A. See Beckmann.
- Kötz, A., derivatives of dichloroquinazolines, i, 372.
- Kohlrausch, F., solutions of sodium silicates, ii, 166.
- Kolk. See Schröder van der Kolk.
- Kolotoff, S., constitution of hydroxylamine, ii, 114.
- saline constituents of water from the Black Sea, ii, 326.
- Kondakoff, I., action of mineral acids on dimethylallene, i, 541.
- action of zinc chloride on fatty alcohols, i, 382.
- composition of commercial amylen, i, 381.
- constitution of angelic and tiglic acids, i, 141.
- oxidation of β -chlorocrotonic acid, i, 549.
- synthesis in the fatty series by means of zinc chloride, i, 382.
- Koninck. See De Koninck.
- Konovaloff, D., electrical conductivity of mixtures, ii, 356.
- Konovaloff, M., derivatives of nonaphthene, i, 196.
- Kooij, D. M., decomposition of gaseous hydrogen phosphide, ii, 569.
- Kormilitzin, A., action of silver oxide on magnesium nitrate, ii, 12.
- Kosmann, B., dehydration of cupric hydroxide and its basic salts, ii, 374.
- minerals from Lower Silesia, ii, 173.
- separation of iron, aluminium, manganese, zinc, and calcium, ii, 600.
- Kossel, A., and F. Freytag, certain chemical constituents of the medulla of nerve, i, 234.
- Kossel, A., and J. Horbaczewski, nucleic acid, i, 680.
- Kossler, A., estimation of hydrochloric acid in the contents of the stomach, ii, 86.
- Kossler, A., and E. Penny, volumetric estimation of phenol in urine, ii, 100.
- Kossovitch, P., fixation of nitrogen by plants, ii, 590.
- Kostanecki, S. v. See Dreher.
- Kottmayer, G., estimation of emetine in ipecacuanha root, ii, 560.
- Krakau, A. A., Meidinger's cells, ii, 355.
- Krapavin, S. See Zelinsky.
- Krauss, E., nutritive value of proteids, ii, 540.
- Krawczynski, S., titration apparatus with automatic zero adjustment, ii, 41.
- Krawkow, N. P., amyloid substance, i, 288.
- chitins, i, 615.
- influence of ligature of the bile duct on metabolism, ii, 329.
- Kreidl, I., estimation of uric acid, ii, 558.
- Kreis, H., modification of the Reichert-Meissl method, ii, 396.
- Kritschenko. See Petrenko-Kritschenko.
- Kromer, N., glucoside of *Ipomœa pandurata* (*Convolvulus pandurata*, L.), i, 482.
- glucosides of the Convolvulaceæ, i, 423.
- Kronberg, H., determination of the molecular weight from the rate of evaporation, ii, 261.
- Krückeberg, F., ethylic azobenzene-cyanacetate, i, 210, 509.
- Krüger, M., constitution of hypoxanthine and adenine, i, 736.
- Krüger, T. R., ethereal hydrogen sulphates from secondary alcohols, i, 495.
- Krüss, G., action of aniline and aniline hydrochloride on the gadolinite earths, ii, 376.
- determination of equivalents by conversion of oxides into sulphates: separation of the gadolinite metals, ii, 283.
- electrolysis of solutions of the rare earths, ii, 284.
- erbia, ii, 376.
- formation of thiovanadates, ii, 379.
- Krüss, G., and H. Krüss, quantitative spectrum analysis, ii, 295.

Krüss, G., and A. Loose, approximate determination of the equivalent of earths by titration, ii, 465.

— behaviour of the gadolinite earths with potassium chromate, ii, 375.

Krüss, G., and H. Moraht, reaction between ferric salts and soluble thiocyanates, i, 185.

Krüss, G., and F. W. Schmidt, action of chlorine and bromine on gold, ii, 474.

— determination of the atomic weight of nickel, ii, 212.

— double halogen compounds of gold, ii, 284.

Krüss, G., and C. Volk, sulphur compounds of thorium, ii, 574.

Krüss, G. See also Hofmann.

Krug, W. H., gravimetric estimation of furfuralhydrazone, ii, 556.

Kruse, H. See Wallach.

Kühling, O., interaction of orth-amidotolylamine and alloxan derivatives, i, 324.

Kühling, O. See also Liebermann.

Kühne, W., albumoses and peptone, i, 233, 741.

Kuenen, J. P., measurements of Van der Waals' surface for mixtures of carbonic anhydride and methylic chloride, ii, 260.

Küster, F. See Zincke.

Kulisch, P., chemical composition of apples and pears especially with regard to their utilisation for fruit wine, ii, 37.

Kunkel, A. J., absorption of iron, ii, 23.

Kunz, G. F., and E. Weinschenk, meteorite from Indian Valley township, Virginia, ii, 80.

— meteorite from the Sierra de la Ternera, Chili, ii, 80.

Kurbatoff, D., presence of linoleic acid in some animal fats, i, 392.

Kuriloff, V., production of hydrogen peroxide in the electrolysis of aqueous sulphuric acid, ii, 108.

— products of the dry distillation of birch bark, i, 131.

Kurnakoff, N. S., influence of hydration on solubility, ii, 509.

— specific heat of carbonic anhydride, ii, 5.

Kutcheroff, M. G., action of mercury salts on unsaturated hydrocarbons and alcohols, i, 450.

Kuthe, M. See Wallach.

Kux, H., gas-volumetric estimation of organic acids and of iodic acid, ii, 307.

Kyle, J. J. J., vanadiferous lignite in the Argentine Republic, ii, 128.

L.

Laborde, J., volumetric estimation of mercury, ii, 495.

Laborde, J. V. See Grimaux.

Lachaud, M., and C. Lepierre, action of hydrogen ammonium sulphate on glass, ii, 280.

— oxidation and sulphonation of organic compounds by ammonium hydrogen sulphate, i, 411.

Ladenburg A., crystalline form of scopoline platinochloride, i, 739.

— isocotine and the asymmetrical nitrogen atom, i, 442.

— resolution of β -pipercoline into its optical isomerides, i, 427.

— synthesis of oxypyridine and oxypiperidine bases, i, 426.

Lafont, J. See Bouchardat.

Lagodzinski, K. See Graebe.

La Harpe. See De la Harpe.

Lajoux, H., and A. Grandval, mercuric salicylates, i, 642.

Lajoux, H. See also Grandval.

Lampe, O. See Michaelis.

Landau, S., mesitylene, i, 32.

Landauer, J., the origin of blow-pipe analysis, ii, 342.

Landolt, H., conservation of mass in chemical changes, ii, 452.

— vapour pressures of fatty acids, ii, 446.

Landolt, H., and H. Jahn, molecular refractive power of organic compounds for infinite wave-length, ii, 57.

Landsteiner, K. See Bamberger.

Langbein, H. See Stohmann.

Lange, O., volume of blood corpuscles, ii, 332.

Lapicque, L., physiological action of iodides, ii, 222.

— physiological action of iodine compounds, ii, 222.

Lapicque, L., and A. Malbec, action of strontium iodide on the circulation, ii, 222.

Lapraik, W., absorption spectra of chromium compounds, ii, 313.

Laquer. See Benno-Laquer.

Laspeyres, H., beyrichite from Altenkirchen, ii, 18.

— cobaltiferous and nickeliferous iron pyrites from Müsen, ii, 18.

Lassar-Cohn, the acids of ox bile, ii, 220, 383.

- Laudenheimer, E. See Paal.
 Lauder, A. See Dobbie.
 Laurent, E. See Schloesing.
 Laurie, A. P., compound of gold and tin, ii, 74.
 Laves, E., analysis of butter, ii, 602.
 — detection and estimation of glucose by means of phenylhydrazine, ii, 555.
 Lea, M. C., dehydration of silver oxide, ii, 11.
 — disruption of silver haloids by mechanical force, ii, 69.
 — nature of certain solutions, and a new means of investigating them, ii, 566.
 — silver, ii, 207.
 — silver chloride, ii, 208.
 — silver hemisulphate, ii, 115.
 Lebedeff, I., transformation of elaidic acid into oleic and isoleic acids, i, 550.
 Le Bel, dimorphism of dimethylamine platinochloride, i, 387.
 Le Bel. See also Combes.
 Le Bel, J. A., alteration of the sign of optical rotation, ii, 255.
 Le Boulenger, P. See Brochet.
 Le Chatelier, A., dioptase from the Congo, ii, 421.
 Le Chatelier, H., dissociation of barium peroxide, ii, 71.
 — dissociation of calcium plumbate, ii, 524.
 — estimation of small quantities of combustible gas mixed with air, ii, 487.
 — fusion of calcium carbonate, ii, 117, 166.
 — heat of formation of arragonite, ii, 259.
 Leduc, A., densities and molecular volumes of chlorine and hydrogen chloride, ii, 410.
 — densities of certain gases and the composition of water, ii, 453.
 — density of carbonic oxide and the atomic weight of carbon, ii, 165.
 — density of nitric oxide, ii, 272.
 — density of sulphurous anhydride, ii, 516.
 — new system of atomic weights, partly based on the direct determination of the molecular weights, ii, 267.
 Leeuwen. See Van Leeuwen.
 Lefèvre, C., crystalline arsenates, ii, 273.
 Léger, E., benzoylcinchonine, i, 678.
 — estimation of benzoyl in organic compounds, ii, 395.
 — hydrogen bromide, ii, 114.
 — volumetric estimation of alkaloïds, ii, 199.
 Léger, E. See also Jungfleisch.
 Lehmann, C., F. Mueller, I. Munk, H. Senator, and N. Zuntz, physiology of starvation, ii, 477.
 Lehmann, V., action of benzoic chloride on ammonia, ii, 145.
 Leidie, E. See Joly.
 Leighton, A. E. See Hannay.
 Leins, H. See Brunner.
 Lellmann, E., and A. Görtz, coefficients of affinity of organic bases, ii, 407.
 Lellmann, E., and N. Mayer, intramolecular formation of the azo-group, i, 201.
 — some nitro- and amido-benzylated bases, i, 198.
 Lellmann, E., and J. Schliemann, coefficients of affinity of organic acids, ii, 407.
 Lemoine, G., decomposition of oxalic acid by ferric salts under the influence of heat, ii, 405.
 — ferric chloride and ferric oxalate solutions, ii, 405.
 Le Neve Foster, E., soda from the alkaline waters of Owen's Lake, ii, 18.
 Lengfeld, F., and E. O'Neill, Californian petroleum, i, 237.
 Lengfeld, F., and J. Stieglitz, nitrogen halogen compounds, i, 310, 631.
 Lenher, V. See Smith.
 Lenoble, E., a reaction of cupric salts, ii, 554.
 Lenormand, C., iron chlorobromide, ii, 377.
 Leo, H. See Friedheim.
 Leonardi, E. See Mazzara.
 Lepereq, G., action of alkali nitrites on alkyl salts of brominated fatty acids, i, 65.
 Lepierre, C., atomic weight of thallium, ii, 322.
 Lepierre, C. See also Lachaud.
 Leroy, J. A., derivatives of α -naphthylacetylene and of β -naphthylacetylene, i, 421.
 Lesage, P., rate of evaporation of solutions of sodium and potassium chlorides, ii, 64.
 Lescoeur, H., dissociation of saline hydrates and analogous compounds, ii, 364.
 — purification of arsenical zinc, ii, 209.
 Lespieau, action of zinc on bromoderivatives of tricarbon nuclei, i, 1.
 Lévy, L., titanium, i, 257.
 — alcoholic fermentation of Jerusalem artichokes with pure yeast, ii, 482.

- Levy. See Magnus-Levy.
 Lewinski, M. See Schröter.
 Lewkowsitch, J., analysis of fats, ii, 310.
 — estimation of resins in soaps, ii, 609.
 L'Hôte, L., preparation of vanadyl trichloride: extraction of vanadium from its ores, ii, 17.
 Lidoff, A., solubility of the lead salts of stearic and palmitic acids in ether, i, 548.
 — the elaidin reaction, ii, 559.
 Liebermann, C., addition of sodium alkyl oxides, i, 583.
 — coca leaves, i, 182.
 — new synthesis of allocinnamic acid, i, 513.
 — optically active cinnamic acid dibromides, i, 582.
 — specific rotatory power of the phenyldibromopropionic acids, i, 268.
 — theory of the formation of coloured compounds with mordants, i, 510.
 — thiophen of crystallisation, i, 406.
 Liebermann, C., and A. Bistrzycki, action of ammonia and hydrazine on opianic and phthalaldehydic acids, i, 371.
 Liebermann, C., and H. Finkenbeiner, optically active cinnamic acid dichlorides, i, 415.
 Liebermann, C., and A. Hartmann, optically active cinnamic acid dibromides, i, 414, 582.
 Liebermann, C., and O. Kühling, hygrineoxime, i, 446.
 Liebermann, C., and H. Sachse, constitution of the truxillic acids, i, 418.
 Liebermann, L., chemistry of the kidney substance, ii, 27.
 — the phosphates of horse's urine, ii, 30.
 Liebermann, L., and S. Bugarszky, diffusion in aqueous solutions of mixed salts, ii, 565.
 Liebermann, L., and S. Székely, estimation of fat in milk, ii, 308.
 Likiernik, A. See Schulze.
 Lilienfeld, L., researches on blood, ii, 22.
 Lilienfeld, L., and A. Monti, microchemical localisation of phosphorus in the tissues, ii, 135.
 Lima. See Mancuso-Lima.
 Limpach, L. See Hodgkinson.
 Limpricht, H., nitrososulphonic acids, i, 168.
 Lindemann and Motteu, detection of alkaloids, "saccharin," and salicylic acid, ii, 606.
 Lindgren, W., and W. H. Melville, sodalite-syenite from Montana, ii, 538.
 Lindner, R., the two isomeric benzyl derivatives of nitroso- β -benzylhydroxylamine, i, 572.
 Lindström, G., brandite and friedelite, ii, 420.
 Linebarger, C. E., dissociation of salts into their ions by water of crystallisation, ii, 265.
 — existence of double salts in solution, ii, 450.
 — Friedel-Crafts reaction in the anthracene series, i, 358.
 — hydrates of manganous sulphate, ii, 417.
 — influence of the concentration of the ions on the intensity of the colour of solutions of salts in water, ii, 203.
 — molecular masses of dextrin and gum arabic as determined by their osmotic pressures, i, 7.
 — paranthracene, i, 357.
 — relations between the surface tensions of liquids and their chemical constitution, ii, 8.
 — solubility of triphenylmethane in benzene, i, 273.
 Ling, A. R., and J. L. Baker, halogen derivatives of quinone. Part III. Derivatives of quinhydrone, TRANS., 1314.
 Linge. See Van Linge.
 Linow, E. See Michaelis.
 Lintner, C. J., formation of dextrose from starch, i, 4.
 Lintner, C. J., and G. Düll, preparation of isomaltose, i, 5.
 Lippert, W., decomposition of ethers by hydrogen haloids, i, 620.
 Lippmann, E., and F. Fleissner, allocinchonine, ii, 738.
 Lippmann, E. O. v., an acid in beet leaves, ii, 85.
 — coniferin, i, 110.
 — dulcitol, i, 64.
 — sorbitol, i, 64.
 Lippmann, E. O. v., and O. Hahn, levulan, i, 63.
 List, O. See Meyer.
 Litthauer, S., substantive cotton dyes from diamidophenanthraquinone, i, 422.
 Liveing, G. D., and J. Dewar, spectra of the flames of some metallic compounds, ii, 401.
 — spectrum of liquid oxygen and refractive indices of liquid oxygen, nitrous oxide, and ethylene, ii, 201.

- Lobry de Bruyn, C. A., methyl and ethyl alcohol as solvents, i, 244.
 — preparation of orthodinitrobenzene, i, 256.
- Locke, F. S., action of sodium oxalate on voluntary muscle, ii, 480.
- Loezka, J., rock salt from Deésakna, ii, 575.
- Lodder, W. See Bamberger.
- Löw, E. See Engler.
- Loew, O., characterisation of sugars, i, 4.
- Loewy, A., action of fatiguing muscular work on the respiratory interchange, ii, 21.
- Löwy, R., tetramethoxydiphthalyl, i, 588.
- Long, J. H., American menthol, i, 223.
 — American oil of turpentine, i, 594.
- Longstaff, G. D., obituary notice of, TRANS., 751.
- Loof, E., constituents of wood oil, i, 558.
- Loomis, E. H., a more exact cryoscopic method, ii, 261.
- Loose, A. See Krüss.
- Lopes, S., detection of hydrocyanic acid, ii, 502.
- Lorenz, N. v., a source of error in the estimation of phosphoric acid by magnesia mixture, ii, 185.
 — behaviour of proteids to concentrated hydriodic acid, i, 379.
- Lorenz, R., estimation of carbon in steel, ii, 491.
- Lorenz, R., and F. Heusler, volatility of manganese at high temperatures, ii, 377.
- Lorenzen, J. See Bamberger.
- Lorimer, W. S., and E. F. Smith, determination of the atomic weight of cadmium, ii, 168.
- Lossen, W., dibromosuccinic acids, i, 142.
 — preparation of silver acetylide from acetylenedicarboxylic acid, i, 121.
 — stereoisomerism of the benzhydr-oxamic acids, i, 572.
- Louguinine, W., specific heat of erythritol and mannitol, ii, 258.
- Louguinine, W., and I. Kablukoff, heat developed by the combination of bromine with non-saturated compounds, ii, 444.
- Lovén, J. M., action of hydrogen sulphide on pyruvic acid, i, 308.
- Low, A. H., estimation of alkalis in silicates, ii, 436.
 — estimation of lead, ii, 437.
 — estimation of manganese in ores, ii, 438.
- Lowe, W. F., gravimetric estimation of zinc as sulphide, ii, 302.
- Low, W. H., estimation of free and combined alkali in soap, ii, 191.
- Lubavin, N., diastase, i, 744.
 — distribution of calcium and magnesium in nature, ii, 373.
- Lucion, M. See Spring.
- Luckow, C., action of potassium permanganate on sodium thiosulphate, ii, 164.
 — volumetric estimations and separations by means of potassium ferrocyanide and ferrieyanide, ii, 242.
- Ludeking, C., and J. E. Starr, specific heat of liquid ammonia, ii, 258.
- Ludwig, E., detection of mercury in the organism, ii, 243.
- Ludwig, E. See also Tschermak.
- Lüder, H., hexametaphosphates, ii, 569.
- Lüdy, F., gum-benzoïn from Siam, i, 666.
 — gum-benzoïn from Sumatra, i, 480.
- Lüttke, J., sensitive litmus indicator, ii, 294.
- Lumière, A., and A. Seyewetz, action of potassium permanganate on organic acids, i, 251.
 — action of sodium sulphite on salts of amidophenols, i, 568.
- Lunge, G., constitution of bleaching powder, ii, 277, 372.
 — estimation of sulphur in roasted pyrites, ii, 187.
 — improvements in gas-volumeters, ii, 41.
- Lunge, G., and F. Bachofen, specific gravity of bleaching powder solutions, ii, 488.
- Lunge, G., and L. Marchlewski, estimation of carbon in iron or steel, also of carbonic anhydride in aqueous solution, ii, 45.
 — influence of nitric peroxide on the specific gravity of nitric acid, ii, 66.
- Lunge, G., and E. Schmid, estimation of oxygen in lead, ii, 302.
- Luxembourg, K. See Michaelis.
- Luzi, W., graphite, ii, 414.
 — graphite and graphitite, ii, 320.

M.

- Macallum, A. B., demonstration of the presence of iron in chromatin by micro-chemical means, ii, 24.
- MacElroy, K. P., and W. D. Bigelow, detection of strontium in presence of calcium, ii, 92.

- MacElroy, K. P., and W. H. Krug, specific gravity of aqueous solutions of acetone, i, 7.
- Macfarlane, W., and A. Wilson, rapid estimation of phosphorus in iron and steel, ii, 596.
- MacGregor, J. See Frankland.
- Mach, H., abietic acid, i, 582.
- Maclaurin, R. C., the dissolution of gold in a solution of potassium cyanide, TRANS., 724.
- Macnair, D. S., a quantitative method of separating iodine from chlorine and bromine, TRANS., 1051.
- Maercker, M., effect of phosphatic manuring on the amount of sugar and the value of beet-root, ii, 228.
- the citrate and molybdate methods for the estimation of soluble phosphoric acid, ii, 237.
- Mager, H., constitution of suberone and of the closed chain ketones of pimelic and azelaic acids, i, 557.
- Maggiore, A., composition of over-ripe cheese, ii, 29.
- Magnanini, G., action of acetylacetone on bromacetone in presence of sodium ethoxide, i, 623.
- influence of boric acid on the electrical conductivity of aqueous solutions of organic acids, ii, 506.
- the colour of the ions, ii, 510.
- Magnanini, G., and M. Scheidt, action of benzaldehyde on the ammoniacal derivatives of dehydrodiacetyllevulinic acid, i, 177.
- Magnus-Levy, A., action of formaldehyde on benzenesulphonamide, i, 714.
- digestibility of milk and bread, ii, 580.
- Magnus-Levy, A. See also Zuntz.
- Mahlke, A., mercurial thermometers to register up to 550°, ii, 443.
- Mahon, R. W., modification of the stannous chloride method of titrating iron, ii, 499.
- Mai, J. See Jannasch.
- Maisch, C. C. See Michael.
- Majert, W., and A. Schmidt, piperazine, PROC., 1893. 35.
- Makins, G. H., obituary notice of, TRANS., 754.
- Malbec, A. See Lapicque.
- Malbot, H., and A. Malbot, action of secondary caprylic iodide on trimethylamine, i, 7.
- Mallard, E., and G. Friedel, melanophlogite, ii, 382.
- Mallet, J. W., Jean Servais Stas, and the measurement of the relative masses of the atoms of the chemical elements, TRANS., 1.
- Mallèvre, A., influence of acetic acid on gaseous metabolism, ii, 21.
- Mamert. See Thomas-Mamert.
- Manasse, O., conversion of nitroso-camphor into camphoric imide: camphordioximes, i, 277.
- Manasse, O. See also Claisen.
- Manby, C. E., estimation of phosphorus, ii, 89.
- Mancuso-Lima, G., estimation of phosphoric anhydride in basic slag, ii, 238.
- Mangold, C., analysis of sealing wax, ii, 148.
- estimation of glycerol, ii, 51.
- Maquenne, L., glyoxalinedicarboxylic acid, i, 281.
- identity of the hydrocarbon C_7H_{14} derived from perseitol and from resin oil with heptanaphthene, i, 635.
- lime-tree honey, i, 618.
- preparation of acetylene, i, 62.
- preparation of tetraiodoethylene, i, 449.
- Mar, F. W. estimation of barium in the presence of calcium and magnesium, ii, 47.
- Marais, J. T. See Thiele.
- Marcet, W., absorption of oxygen and formation of carbonic anhydride in human respiration, ii, 20.
- exercise and respiratory exchange, ii, 579.
- Marchal, C., and J. Wiernik, separation of iron, aluminium, and chromium, ii, 49.
- Marchetti, G., cryoscopic behaviour of aqueous solutions of chromium chlorides, ii, 122.
- pyrazole derivatives, i, 179.
- pyrazole-3 : 5-dicarboxylic acid, i, 674.
- reduction of 1 : 3 : 5-phenyldimethylpyrazole, i, 178.
- reduction of 1 : 4 : 5-phenylmethylpyrazole, and 1 : 3 : 5-phenyldimethylpyrazole, i, 177.
- reduction of substituted 1-phenylpyrazoles, i, 673.
- Marchetti, G. See also Balbiano.
- Marchis, L., mixtures of ether and water, ii, 264.
- Marchlewski, L., gas-volumetric estimation of iodine, ii, 144.
- methods of estimating sulphur, ii, 551.
- nitrous acid in nitric acid, ii, 206.
- Marchlewski, L., rate of diffusion of dextro- and lævo-rotatory tartaric acid, ii, 316.

- Marchlewski, L., the constitution of rubiadinglucoside and rubiadin, *TRANS.*, 1137.
- the existence of nitrous acid in aqueous solution, ii, 569.
- Marchlewski, L., and J. Sachs, new formation of basic sulphates of copper, ii, 169.
- — Roussin's salt, ii, 211.
- Marchlewski, L. See also Lunge, Schunck.
- Marchlewski, L. P., methods of estimating the sulphur in sulphides, ii, 186.
- Marckwald, W., amido- and nitro-derivatives of pyridine, i, 727.
- stereoisomeric thiosemicarbazides, i, 26.
- Marckwald, W., and A. Ellinger, a derivative of amidoacetal, i, 213.
- — glycolaldehydes, i, 7.
- Marckwald, W., and P. Wolff, diphenylanilguanidine, i, 25.
- Marckwald, W., and others, constitution of cycloid systems, i, 603.
- Marckwald, W. See also Wohl.
- Marcusson, J. See Meyer.
- Markovnikoff, V., action of bromine on closed-chain hydrocarbons in presence of aluminium bromide, i, 13.
- heptonaphthene (hexahydrobenzoic) acid, i, 93.
- suberene, i, 13.
- Markovnikoff, V., and A. Reformatsky, Bulgarian (Turkish) oil of roses, i, 662.
- Marouby, detection of adulteration in wines, ii, 501.
- Marpurgo, J., detection of nitrobenzene, ii, 306.
- Marsh, J. E., and J. A. Gardner, researches on the terpenes. Part III. The action of phosphorus pentachloride on camphene, *PROC.*, 1893, 163.
- Marshall, W. See Purdie.
- Martelli, D., estimation of phosphoric anhydride in basic slag, ii, 238.
- Martin, E. See Grehan.
- Martin. See De Saint Martin.
- Martius, F., occurrence of hydrochloric acid in the stomach, ii, 540.
- Mason, A. T., piazine (pyrazine) derivatives. Part II. *TRANS.*, 1284.
- preparation of mono-, di-, and tri-benzylamine, *TRANS.*, 1311.
- Mason, A. T., and L. A. Dryfoos, condensation products from ethylenediamine, and derivatives of acetoacetic acid, *TRANS.*, 1310.
- — piazine derivatives. Part III, *TRANS.*, 1293.
- Mason, A. T., and G. R. Winder, synthesis of piazine derivatives: inter-
- action of benzylamines and phenacyl bromide, *TRANS.*, 1355.
- Massau, C. See Claus.
- Masson, active principles of bryony root, i, 424.
- Matignon, C., general results of the thermochemical study of the ureides, ii, 362.
- dehydroxyamalic acid, i, 405.
- hydurilic acid, i, 149, 405.
- thermochemical investigation of polybasic ureides and of uric acid, ii, 360.
- thermochemical investigation of ureides derived from acids containing 2 carbon atoms, ii, 358.
- Matignon. See Berthelot.
- Matthey, E., metallurgy of bismuth, ii, 534.
- Maull, C. See Rupe.
- Maumené, E., ammonium chromates, ii, 17.
- preparation of mucic acid from gum arabic, i, 628.
- Mauro, F., fluoroxymolybdates: the non-existence of cuprous fluoride, ii, 124.
- Mauthner, J., physiological action of asparagine, ii, 27.
- Maxwell, W., phosphorus and the lecithins, ii, 289.
- Mayer, A., influence of sugar on the constitution of milk fat, ii, 27.
- melting point and composition of butter from cows variously fed, ii, 28.
- production of albumin in plants, ii, 224.
- Mayer, F. See Witt.
- Mayer, N. See Lellmann.
- Mazzara, G., unsymmetrical dibenzylthiocarbamide, i, 411.
- Mazzara, G., and E. Leonardi, acetylnitrocarbazole, i, 213.
- — carbazole, i, 349.
- Meerburg, J. H., permeability of precipitated membranes, ii, 367.
- Meimberg, F. See Bamberger.
- Meineke, C., cyanogen iodide and sodium thiosulphate, ii, 246.
- detection of cyanogen in iodine, ii, 246.
- estimation of cyanogen in iodine, ii, 246.
- preparation of pure iodine, ii, 204.
- Meister, H., metahydroxyvitic acid, i, 252.
- Meldola, R., the action of nitrous acid on 1-amido-2-naphthol, *PROC.*, 1892, 218.
- Meldola, R., and F. B. Burls, azo-compounds of the ortho-series, *TRANS.*, 930.

- Meldola, R., and F. B. Burls, note on a meta-azo-compound, *Proc.*, **1893**, 126.
- Meldola, R., and M. O. Forster, the preparation of dinitronaphthylamine [$\text{NH}_2 : (\text{NO}_2)_2 = 1 : 2 : 4$] from its acetyl and valeryl derivatives, *Proc.*, **1893**, 7.
- Meldola, R., and E. M. Hawkins, azo-compounds of the ortho-series, *Trans.*, 923.
- Meldola, R., and F. W. Streatfeild, some peri-derivatives of naphthalene, *Trans.*, 1054.
- Melikoff, P., analysis of the Wawilowka meteorite, *ii*, 579.
- Melikoff, P., and C. Schwalbe, meteorite of Grossliebenthal, *ii*, 216.
- Melville, W. H., josephinite, a new nickel-iron, *ii*, 75.
- Melville, W. H. See also Lindgren.
- Menschutkin, N., influence of the constitution of the alcohols on the velocity of etherification, *ii*, 158.
- Merck, E., adonite, *i*, 481.
- alkaloids from *Corydalis cava*, *i*, 492.
- champacol, a new camphor, *i*, 480.
- crystallised veratrine, *i*, 490.
- hydrastinine hydrogen tartrate, *i*, 491.
- hyoscyamine, *i*, 491.
- pseudohyoscyamine, *i*, 491.
- relation between atropine, apotropine, and belladonnine, *i*, 491.
- Merling, G., action of hydrogen peroxide on piperidine bases, *i*, 113.
- Meslans, M., action of anhydrous hydrogen fluoride on alcohols, *i*, 186.
- estimation of fluorine in combustible gases, *ii*, 488.
- Messinger, J. See Kehrmann.
- Metcalf, W. V., action of alcohols on paradiazotoluenemetasulphonic acid, *i*, 585.
- Metzner, R. See Ditte.
- Meunier, S., meteoric iron from Augustinowka (Russia), *ii*, 423.
- meteoric iron from Hassi Jekna, Algeria, *ii*, 79.
- two Turkish meteorites, *ii*, 578.
- Meyenburg, F. v., synthesis of α -phenylindoxazen, *i*, 587.
- Meyer, L., a small air thermometer for laboratory use, *ii*, 357.
- Köhnlein's method of preparing paraffins: properties of propane, *i*, 681.
- lectures on inorganic chemistry arranged in accordance with the natural system of the elements, *ii*, 408.
- Meyer, L., magnesium diphenyl, *Proc.*, **1893**, 111.
- spectroscopical investigation of salts of aromatic bases, *i*, 464.
- Meyer, L., jun., phenazone, *i*, 733.
- separation of phenyldibromopropionic acid into its optically active modifications, *i*, 93.
- Meyer, P., bromination of phenylhydrazine, *i*, 155.
- Meyer, R., compounds of phthalic acid with phenols, *i*, 275.
- Meyer, R., and E. Saul, action of phenylhydrazine on lactones, *i*, 473.
- the fluorescein group, *i*, 220.
- xanthydrol, *i*, 471.
- Meyer, R., J. See Friedheim.
- Meyer, V., iodoso-compounds, *i*, 713.
- substitution in aliphatic acids, *i*, 64.
- temperature of explosion of gaseous mixtures, *ii*, 258.
- Meyer, V., O. List, J. Marcusson, and W. A. Bone, indoxazen derivatives, *i*, 469.
- Meyer, V., and P. Petrenko-Kritschenko, action of bromine on ethylic chloride and certain butane derivatives, *i*, 62.
- Meyer, V. See also Askenasy, Bodenstein, Cathcart, Freyer, Hartmann.
- Meyerhoffer, W., a new double salt, *ii*, 119.
- cryohydric quintuple points, *ii*, 447.
- the number of saturated solutions of a double salt, *ii*, 449.
- Meyerhold, F. A., acid reaction of muscle, *ii*, 176.
- Michael, A., action of diazobenzene-imide on methylic acetylenedicarboxylate, *i*, 570.
- addition of bromine to acetylenedicarboxylic acid and its ethylic salt, *i*, 144.
- comparison of experimental results with the theoretical conclusions of the Van't Hoff-Wislicenus hypothesis, *i*, 145.
- ethylic sodacetoacetate, *i*, 67.
- formation of solid crotonic acids by the reduction of α -isobromo- and α -isochloro-crotonic acids, *i*, 134.
- new apparatus, *ii*, 267.
- Michael, A., and C. C. Maisch, action of sodium ethoxide on ethylic dibromosuccinate, *i*, 142.
- Michael, A., and O. Schultess, crotonic acids and their derivatives, *i*, 132.

- Michael, A., and G. Tissot, addition of chlorine to polybasic unsaturated fatty acids, i, 142.
- homologues of malic acid, i, 146.
- Michael, Mrs. H. A., addition of bromine and chlorine to solid crotonic acid, i, 134.
- Michael, R., paraxylidine, i, 198.
- Michaelis, A., action of chlorides of bibasic acids on hydrazines, i, 705.
- thionylamines, i, 504.
- Michaelis, A., and R. Hermens, β -succinylphenylhydrazide or 1-phenyl-3:6-orthopiperazine, i, 370.
- Michaelis, A., and W. Jacobi, thionylamines of unsaturated bases: thionylphenylpropylamine, i, 702.
- Michaelis, A., and O. Lampe, phenylpyrazolidine, i, 611.
- Michaelis, A., and K. Luxembourg, derivatives of unsymmetrical allylphenylhydrazine and allyltolylhydrazine, i, 704.
- Michaelis, A., and G. Schröter, thionylbenzylhydroxylamine and dibenzoxycarbamide, i, 702.
- Michaelis, A., G. Schröter, and E. Linow, action of thionyl chloride on benzylamine and its homologues, i, 703.
- Michaelis, A., and H. Siebert, action of thionyl chloride on acid amides, i, 553.
- Michaelis, A., and O. Storbeck, action of thionyl chloride on benzylamine, i, 515.
- thionylamines of the aromatic series, i, 504.
- thionyl-diethylhydrazone, i, 249.
- Michaelis and others, thionylamines of the aliphatic series, i, 515.
- Michaelis, L., bromination of aromatic hydrazines and amines, i, 705.
- Michaud, G., and J. F. Tristan, agavose, i, 64.
- Michel, L., artificial production of garnet (melanite) and sphene, ii, 129.
- artificial production of rutile, ii, 173.
- Michel, O., and E. Grandmougin, acetyl derivatives of 2:1-amidonaphthol, i, 171.
- Michel, O. See also Noeltling.
- Michels, W., seleno- and thio-derivatives of ethylamine, i, 30.
- Michels, W. See also Gabriel.
- Mijers, J., constitution of bleaching powder, ii, 209, 372.
- Miklascheffsky, S., hydration of ethylenic hydrocarbons, i, 61.
- Millar, J. H. See Tilden.
- Miller, L., transformation of chemical into electrical energy, ii, 107.
- Miller, O., estimation of indigotin in commercial indigo, ii, 352.
- Miller, W. v., and J. Plöchl, amid-oxalic acids, i, 502.
- Minguin, J., bromal borneolates, i, 526.
- Minunni, G., α -benzilephenylhydrazine and the oxidation of the hydrazones, i, 97.
- condensation of β -benzoylphenylhydrazine with aldehydes, i, 86.
- constitution of isomeric aliphatic oximes, i, 188.
- formation of benzonitrile from α -benzaldoxime, i, 89.
- isomerism of oximes, i, 89.
- preparation of benzoic anhydride: formation of dehydracetic acid from acetic chloride, i, 92.
- Minnuni, G., and G. Corselli, action of phenylhydrazine on some isomeric aldoximes, i, 87.
- action of phenylhydrazine on the benzoyl derivatives of some α -aldoximes, i, 88.
- determination of the structure of the oximido-group in the ethers of the oximes, i, 87.
- Minunni, G., and G. Ortoleva, benziloximes, i, 97.
- Miolati, A., paramagenta, i, 572.
- synthesis of mercaptothiazoles, i, 634.
- thiocyanacetamide and isothiohydantoïn, i, 405.
- Miolati, A. See also Hantzsch, Werner.
- Mitchell, C. A., black antimony trisulphide, ii, 473.
- Mitscherlich, A., the ignition point, ii, 202, 257.
- Mittelmeier, H. See Scheibler.
- Mixter, W. G., behaviour of charcoal with halogens, nitrogen, sulphur, and oxygen, ii, 571.
- Möhlau, R., and R. Berger, introduction of the phenyl group into cycloïd compounds, i, 701.
- phenylnaphthalenes and Zincke's hydrocarbon $C_{16}H_{12}$, i, 522.
- Möhlau, R., and E. Fritzsche, formation of acridine dyes, i, 470.
- Mörner, C. T., action of drugs containing iron, ii, 427.
- proteïds of the crystalline lens, ii, 424.
- Mohrberg, C., cephalanthin, i, 112.
- Moissan, H., action of a high temperature on metallic oxides, ii, 167.

- Moissan, H., estimation of boron, ii, 435.
 — fusion and volatilisation of metals and oxides in the electric arc, ii, 507.
 — graphite, carbonado, and microscopic diamonds in blue earth from the Cape, ii, 285.
 — intumescent graphite, ii, 320.
 — iron from Ovifak, ii, 475.
 — opium smoke, i, 226.
 — physical constants of fluorine, ii, 204.
 — preparation of carbon under high pressure, ii, 275.
 — preparation of chromium and manganese at a high temperature, ii, 281.
 — preparation of tungsten, molybdenum, and vanadium in the electric furnace, ii, 471.
 — preparation of uranium at a high temperature, ii, 283.
 — properties of diamonds, ii, 319.
 — the ash of diamonds, ii, 319.
 — the meteorite from Cañon Diablo, ii, 288.
 — volatilisation of zirconia and silica at a high temperature, and their reduction by carbon, ii, 532.
 Moissan, H., and H. Gautier, specific heat of boron, ii, 404.
 Moissan, H., and J. Violle, an electrical furnace, ii, 314.
 Moitessier, J. See Bertin-Sans.
 Molinari, E., stereochemistry or motorchemistry? ii, 513.
 Molisch, A., iron in plants, ii, 484.
 Moll, F. See Nietzki.
 Monfet, L. See Petit.
 Monnet, P., anisolines, i, 274.
 Montemartini, C., combustion of hydrogen in nitrous oxide, ii, 113.
 — reaction between nitrites and the salts of hydroxylamine, ii, 160.
 Monti, A. See Lilienfeld.
 Moody, G. T., studies on isomeric change. Part II. Orthoxylenesulphonic acids, *Proc.*, 1892, 213.
 — studies on isomeric change. Part III. Phenetolsulphonic acids, *Proc.*, 1892, 214.
 Moody, H. R. See Talbot.*
 Moore, S. L. M., supposed presence of albumin in the walls of vegetable cells, ii, 180.
 Moore, T., assay of tin ore, ii, 501.
 Moraht, H., titration of ferric salts, ii, 193.
 Moraht, H., and C. Wischin, osmium, ii, 380.
 Moraht, H. See Krüss.
 Morat, J. P., and M. Doyon, physiological action of atropine and pilocarpine, ii, 222.
 Moreau, B., precipitation of phosphates and arsenates by ammonium molybdate, ii, 45.
 Morgan, J. J. See Parry.
 Morgernstern and A. Pavlinoff, estimation of phosphoric acid in wines, ii, 389.
 Moroziewicz, J., synthesis of minerals, ii, 422.
 — synthesis of minerals of the hauyn group, ii, 19.
 Morris, G. H. See Brown.
 Moschatos, H., and B. Tollens, additive products and compounds of hexamethylenamine, i, 298.
 Moses, A. J., ettringite and alabandine from Arizona, ii, 578.
 — ettringite from Tombstone, Arizona, ii, 536.
 Motteu. See Lindemann.
 Moureu, acrylamide, i, 695.
 — acrylic anhydride, i, 688.
 — acrylonitrile, i, 682.
 — action of acrylic chloride on alcohols and phenols, i, 688.
 — new method for preparing acrylic acid, i, 548.
 — substituted acrylamides, i, 695.
 Moyer, J. B. See Smith.
 Mühlhäuser, O., boron carbide, ii, 570.
 — higher nitro-derivatives of starch, i, 6.
 Müller, A. See Töhl.
 Mueller, F. See Lehmann.
 Müller, M., distillation apparatus for analysis, ii, 487.
 Müller, R., α -phenylcinnamic acid, i, 341.
 Müntz, A., and H. Coudon, ammoniacal fermentation in soils, ii, 291.
 Müntz, A., and A. C. Girard, loss of nitrogen in manures, ii, 181, 228.
 Muirhead, A. See Abel.
 Mulder, E., ketonic compound from tartaric acid, i, 685.
 Muller J. A., estimation of nitrogen in soils by Kjeldahl's method, ii, 43.
 — estimation of the dry residue in wines, ii, 501.
 — new accessory to Lunge's gas-volumeter, ii, 229.
 — new gas-volumeter, ii, 230.
 Muller, P. T., ethylic phthalocyanacetate, i, 467.
 Muller, P. T. See also Hausser.
 Muller, T., action of chlorides of bibasic acids on ethylic sodiocyanacetate, i, 143.

Mulliken, S. P., organic electrosyntheses, i, 630.
 Munk, I. See Lehman.
 Murray, T. S. See Japp.
 Muthmann, W., preparation of barium permanganate, ii, 324.
 — preparation of pure rubidium salts, ii, 321, 414.
 — red phosphorus, ii, 458.
 Muthmann, W., and J. Schäfer, selenium compounds, ii, 318.
 Myers, W. S. See Collie.

N.

Naccari, A., osmotic pressure, ii, 513.
 Napieralski, B. See Bischler.
 Nasini, R., refractive powers for a ray of infinite wave-length, ii, 505.
 Nasini, R., and A. Pezzolato, decomposition of salts of nicotine and the action of alcohol on them, i, 444.
 Nastiukoff, A., colorimetric analysis of phosphorites, ii, 553.
 — Witz's oxycellulose, i, 387.
 Natterer, K., water and sea-bottom deposits of the Eastern Mediterranean, ii, 216.
 Naupert, A., and W. Wense, minerals occurring in the Westeregeln salt beds, ii, 325.
 Nef, J. U., ethylic acetoacetate, i, 628.
 Neger, F. See Pechmann.
 Negovoroff, A., amine from dextromenthone, i, 224.
 Neher, F., precipitation of arsenic as pentasulphide, and its separation from bismuth, lead, cadmium, and antimony, ii, 186.
 Neitzel, E., titration of acids by metallic sodium, ii, 550.
 Nemirovsky, A., isomeric bromanilines, i, 21.
 Nencki, M., composition of hæmatin and of hæmatoporphyrin, i, 743.
 Nencki, M., and H. Boutmy, influence of the carboxyl group on the toxic action of aromatic compounds, ii, 178.
 Nernst, W., participation of a solvent in chemical reactions, ii, 367.
 Nernst, W. and C. Hohmann, formation of amylic salts from acids and amylene, i, 449.
 Neubauer, H., estimation of phosphoric acid as magnesium pyrophosphate, ii, 236, 489.
 Neubert, C., azo- and hydrazo-benzyl alcohols, i, 200.
 Neumann, A. See Gabriel.
 Neumann, G., action of hydriodic acid on cinchonidine, i, 231.
 Neve Foster. See Le Neve Foster.
 New, C. H., estimation of nitrogen in coal gas, ii, 296.
 Newmann. See Salazar.
 Niccoli, L. See Antony.
 Nickel, E., determination of stereoisomerides, i, 681.
 — graphochemical calculation, ii, 278, 464.
 — graphochemistry of compounds C_nH_mOp , i, 185.
 — graphochemistry of gunpowder, ii, 115.
 — graphochemistry of lime-soda glasses, ii, 119.
 Nicolas, C., sulphur compounds in mineral waters of Barèges, ii, 326.
 Niebel, W., detection of horse flesh in food, ii, 312.
 Niementowski, S., diazoamido-compounds, i, 201.
 Nietzki, R., and A. Bossi, oxazine dyes, i, 44.
 Nietzki, R., and F. Moll, derivatives of phloroglucinol, i, 699.
 — dinitrocatechol and its conversion into nitranilic acid, i, 699.
 Nietzki, R., and E. Rehe, dinitrochlorotoluene and the synthesis of azine dyes, i, 15.
 Nietzki, R., and R. Zehnter, benzeneazonnaphthalene and tolueneazonnaphthalene, i, 275.
 Nihoul, E., estimation of bromine and iodine in presence of chlorine, ii, 42.
 — estimation of iron by an iodometric method, ii, 439.
 — estimation of sugars by means of Fehling's solution, ii, 601.
 Niles, E. P., antiseptic treatment of wounds, ii, 223.
 Nilson, L. F. See Killgren.
 Nobbe, F., and L. Hiltner, how are nodule-bearing Leguminosæ enabled to utilise free atmospheric nitrogen? ii, 588.
 Nobbe, F., E. Schmid, L. Hiltner, and E. Hotter, physiological meaning of the root nodules of *Elæagnus angustifolius*, ii, 33.
 — — — the power of propagation of the leguminous bacteria in soils, ii, 32.
 Noël-Paton, D., crystalline globulin occurring in human urine, ii, 290.
 — influence of fever on hepatic glyco-gen, ii, 541.
 Noelting, E., E. Grandmougin, and O. Michel, formation of hydrogen

- nitride (azoimide) from aromatic azoimides, i, 90.
- Noelting, E., and O. Michel, action of diazo-compounds on hydrazines, i, 202.
- conversion of amines into diazoimides by means of azoimide, i, 202.
- Noelting, E. See also Witt.
- Norden, C. v., alcohol as a substitute for albumin under various conditions of feeding, ii, 328.
- Nordenskiöld, A. E., molecular weight of gadolinium oxide, ii, 211.
- Nordenskiöld, native iron of Ovifak and the bitumen in the crystalline rocks of Sweden, ii, 326.
- Nordenskiöld, G., pholidolite from Sweden, ii, 174.
- Nordenskiöld, O., thiocyanates of chromammonium compounds, i, 290.
- Norton, L. M., estimation of chlorine in electrolysed solutions, ii, 41.
- Norwall. See De Norwall.
- Norwall, F. K. v. See Skraup.
- Nothnagel, G., muscarine, i, 297.
- Noyes, A. A., dissociation ratio of salts, ii, 565.
- electrolytic dissociation of acid salts, ii, 365.
- Noyes, A. A., and A. A. Clement, electrolytic reduction of nitrobenzene dissolved in sulphuric acid, i, 406.
- O.**
- Oberholtzer, V. See Smith.
- Oddo, G., camphor, i, 422.
- isonitrosocamphor, i, 660.
- Oddo, G., and G. Ampola, mixed naphthyl-azo-compounds, i, 655.
- Oesterele, O., guttapercha, i, 224.
- Offermann, H., detection and estimation of thiocyanates in ammonium sulphate, ii, 556.
- Olasavasky, V. See Klug.
- Oliver, T., and F. C. Garrett, gases of blood during anaesthesia, ii, 540.
- Oliviero. See Bouchardat.
- Olszewski, K., and A. Witkowski, optical properties of liquid oxygen, ii, 353.
- Omelyansky, V., influence of dilution on the velocity of chemical reactions, ii, 510.
- O'Neill, E. See Lengfeld.
- Ono, H. See Shimoyama.
- Ordonneau, C., calcium tartrate from distillery residues, its estimation and purification, ii, 558.
- Orndorff, W. R., and C. G. Hopkins, decomposition of diazobenzene sulphate in isoamyl alcohol, i, 639.
- Orndorff, W. R., and J. White, molecular weight of hydrogen peroxide and of benzoyl peroxide, i, 579.
- Orndorff, W. R., and S. W. Young, condensation products of acetone with concentrated sulphuric acid, i, 498.
- Ortoleva, G. See Minunni.
- Orton, E., quartz boulder in Ohio coal, ii, 78.
- Osborne, T. B., crystallised vegetable proteids, i, 380.
- proteids of linseed, ii, 292.
- Osborne, T. B., and C. G. Voorhees, proteids of wheat, i, 741.
- Oser, W. See Bischler.
- Ost, H., estimation of fluorine in the ashes of plants, ii, 234.
- Ostwald, W., discoverer of the method of determining the density of solids by suspension, ii, 508.
- electrolytic dissociation of water, ii, 365.
- thermochemistry of the ions, ii, 357.
- O'Sullivan, J., Dumas' method for estimating nitrogen, ii, 297.
- Otto, R., anilides of benzenesulphonic and paratoluenesulphonic acids, i, 416.
- preparation of pure ethylic benzenesulphinate and ethylic paratoluenesulphinate, i, 270.
- reactions of phenylic iododichloride and iodosobenzene, i, 256.
- Otto, R., and A. Rössing, ethereal sulphinates, i, 343.
- Otto, R., A. Rössing, and J. Tröger, sulphonic derivatives of naphthalene, i, 276.
- Otto, R., and J. Tröger, constitution of glyoxylic acid, i, 141.
- constitution of the iodides of aromatic sulphonic acids, i, 269.
- diphenylsulphone and ditolylsulphone ethyl ethers, i, 415.
- non-existence of Stenhouse's phenylthiosulphuric acid: sulphonic acids of phenyl sulphide: Bunte's salt, i, 416.
- synthesis of symmetrical diphenylsulphoneacetone by means of symmetrical dichloracetone, i, 167.
- Otto, R., and G. Zuschlag, chemical behaviour of ethereal salts of sulphonic acids, i, 344.
- Ouvrard, L., arsenic and antimony iodosulphides, ii, 533.

- Ouvrard, L., arsenic chlorosulphides and antimony chlorosulphides, ii, 533.
 — phosphorus iodosulphide, ii, 164.
 Overton, B., stereochemical phenyl- and diphenyl-hydrzones, i, 208.
 Owens, W. G., meteorite from Central Pennsylvania, ii, 80.

P.

- Paal, C., hyponitrous acid, ii, 372.
 Paal, C., and A. Bodewig, orthonitrobenzyl alcohol, i, 20.
 Paal, C., and E. Fritzweiler, orthonitrobenzylmetamidobenzoic acid, i, 209.
 — — — 2-paratoly lindazole, i, 46.
 Paal, C., and E. Laudenhaimer, action of carbon bisulphide on orthamidobenzyl alcohol, i, 25.
 — — — orthamidobenzyl alcohol and its derivatives, i, 23.
 — — — synthesis of 2-dimethylhydri-ndole, i, 37.
 Pagliani, S., specific conductive capacities and refraction constants, ii, 505.
 Palladin, W., ash in etiolated leaves, ii, 140.
 Panfiloff, I., ethylmethylpropylethylene glycol, i, 545.
 Panormoff, A., formation of ethereal salts of benzoic acid from alcohols and carbohydrates, i, 186.
 — sugar in muscle, ii, 383.
 Papendieck, A. See Buchner.
 Pařízek, A. P., and O. Šule, applications of Raoult's law at the boiling points of solutions, ii, 406.
 Parks, R. M., action of methyl alcohol on paradiazotolueneorthosulphonic acid, i, 585.
 Parlato, E. See Anschütz.
 Parry, J., and J. J. Morgan, analysis of iron and steel, ii, 499.
 Parsons, C. L., comparison of methods for the standardisation of acid and alkaline solutions, ii, 232.
 — potassium tetroxalate, ii, 233.
 Partheil, A., cytosine and ulexine, i, 119.
 — estimation of the volatile fatty acids in butter fat, ii, 197.
 Paschkowetzky, S., magnesium nitride, ii, 209.
 Passerini, N., composition of chick-peas (*Cicer arietinum*): presence of boron, lithium, and copper in the plant, ii, 226.
 — composition of *Iris germanica*: presence of boron, lithium, and copper in the plant, ii, 227.
 Passerini, N., composition of the stems and leaves of tomatoes: presence of boron, lithium, and copper in the plant, ii, 225.
 Passmore, F. W. See Helbing.
 Paton. See Noël-Paton.
 Patry, A. See Pictet.
 Patterson, L. G., estimation of butter fat in milk, ii, 252.
 Paturel, G. See Boiret.
 Paul, T., estimation of antimony and the use of the Gooch filter, ii, 90.
 Pavlinoff, A. See Morgernstern.
 Pavloff, D. See Grigorovitch.
 Payne, H. L., preparation of standard iodine solution, ii, 234.
 Pearce, R., crystalline compound of arsenious and sulphuric anhydrides, ii, 66.
 Pearce, S. H. See Penfield.
 Pears, A., composition of a specimen of jute fibre produced in England, TRANS., 964.
 Pease, F. N. See Dudley.
 Péchard, E., combination of molybdates with sulphurous acid, ii, 530.
 — combination of oxalic acid with titanio and stannic acids, i, 625.
 — combination of selenious acid with molybdates: molybdoselenious acid, ii, 530.
 Péchard, E. See also Baubigny.
 Pechmann, H. v., action of diazobenzene on malonic acid, i, 82.
 — aromatic diazo-compounds, i, 154.
 — Bülow's reaction and the oxidation of hydrzones, i, 461.
 — coumalinic acid, i, 401.
 — mixed azo-compounds, i, 84.
 Pechmann, H. v., and F. Neger, action of acetic anhydride on acetonedicarboxylic acid, i, 398.
 Pechmann, H. v. See also Henry.
 Pélabon, H., absorption of hydrogen selenide by liquid selenium at high temperatures, ii, 457.
 Pellacani, F., derivatives of dibromothymol, i, 316.
 Pemberton, H., jun., and G. P. Tucker, deposits of native soda near Laramie, Wyoming, ii, 535.
 Penfield, S. L., cookeite from Paris and Hebron, Maine, ii, 538.
 — three supposed new sulphides of iron and nickel, ii, 535.
 — xenotime from El Pasco Co., Colorado, ii, 537.
 — zunyite from Colorado, ii, 538.
 Penfield, S. L., and S. H. Pearce, polybasite and tennantite from Aspen, Colorado, ii, 75.
 Penfield, S. L. See also Wells.

- Penny, E. See Kossler.
- Peratoner, A., action of iodine on derivatives of acetylene, i, 2.
- decomposition of the ethylic salts of some chloro- β -ketonic acids by dilute sulphuric acid, i, 11.
- phenylacetylene diiodide, i, 18.
- phenyliodoacetylene, i, 19.
- Peratoner, A., and G. Siringo, action of carbonyl chloride on sodio-phenylhydrazine, i, 24.
- Perkin, A. G., constituents of the Indian dye-stuff kamala, TRANS., 975.
- hexanitroxanilide, TRANS., 1063.
- Perkin, A. G., and J. J. Hummel, the colouring and other principles contained in chay root, TRANS., 1160.
- the colouring principles of *Rubia sikkimensis*, TRANS., 1157.
- Perkin, W. H., the magnetic rotation and refractive power of ethylene oxide, TRANS., 488.
- magnetic rotation of sulphuric acid and nitric acid and their aqueous solutions, also of solutions of sodium sulphate and lithium nitrate, TRANS., 57.
- Perkin, W. H., jun., sulphocamphylic acid, PROC., 1893, 109.
- tetramethylene-derivatives, i, 693.
- Perkin, W. H., jun., and G. Révay, synthesis of indene and hydrindene, i, 716.
- Perkin, W. H., jun. See also Haworth.
- Perlmutter, A., action of nascent hydrogen on quinolinic acid, i, 176.
- Perrault, A., volumetric estimation of chromium, ii, 194.
- Perrier, G., metallic compounds of the benzene series, i, 508, 578.
- Pesch. See Van Pesch.
- Pesci, L., methylphenylmercurammonium hydroxide and salts, i, 24.
- Petermann, A., amount of starch in different varieties of potatoes, ii, 430.
- the nitrogen question, ii, 33, 291.
- Petermann, A., and J. Graftian, carbonic anhydride in the air, ii, 67.
- combined nitrogen in rain, ii, 548.
- Petersen, E., double halogen compounds of gold, ii, 126, 474.
- heat of dissociation of some acids, ii, 259.
- Petersen, J., cryoscopy, &c., of ammonio-metallic compounds, ii, 156.
- estimation of hydrazine in hydrazine salts, ii, 605.
- Petit, A., and L. Monfet, estimation of organic nitrogen, ii, 343.
- Petit, P., calcium sucrates, i, 451.
- vegetable nuclein, i, 539.
- Petrenko-Kritschenko, P., palladium sulphides, ii, 475.
- Petrenko-Kritschenko, P. See also Meyer.
- Pettersson, O., anhydrous chlorides of metals of the rare earths, ii, 466.
- Pettersson, O., and A. Smett, estimation of carbon in iron and steel, ii, 491.
- Pezzolato, A. See Nasini.
- Pfeiffer, T., and G. Kalb, deposition of albumin during the fattening of full grown animals, ii, 25.
- Pflüger, E., estimation of glycogen, ii, 601.
- nutrition with carbohydrate and flesh, and with carbohydrate alone, ii, 327.
- origin of fat from proteid in the body, ii, 327.
- Philipp, C., condensation products of amidophenols and amidophenyl ethers with aldehydes and ketones, i, 78.
- Philips, A. See Graebe.
- Phinney, J. I., treatment of barium sulphate in analysis, ii, 552.
- Phinnuey, J. I. See also Gooch.
- Phipson, T. L., fluorine in fossil wood, ii, 76.
- identity of cascarin and rhamnoxanthin, i, 113.
- Phokin, S., oxidation of diallyloxalic acid by potassium permanganate, i, 12.
- Phookan, R. D., speed of vaporisation of compounds in different atmospheres, ii, 564.
- Piccin, A., action of hydrogen peroxide on certain fluorides and oxyfluorides, ii, 124, 213.
- Piccinini, A., and G. Ruspaggiari, mercuranilido-compounds, i, 322.
- Pichard, P., greater assimilability of the nitrogen of recently-formed nitrates, ii, 548.
- Pickardt, M., detection of dextrose in blood, ii, 81.
- Pickell, J. M., and J. J. Earle, analyses of oranges, ii, 227.
- Pickering, J. W., physiology of the embryonic heart, ii, 424.
- proteid reactions, i, 615.
- Pickering, S. U., a study of the properties of some strong solutions, TRANS., 998.
- cryoscopic behaviour of weak solutions. Parts V, VI, and VII, ii, 110.
- density of sulphuric acid solutions, ii, 155.

- Pickering, S. U., diffusion of substances in solution, ii, 155.
 — freezing points of sodium chloride solutions, ii, 365, 565.
 — isolation of two predicted hydrates of nitric acid, TRANS., 436.
 — note on the stereoisomerism of nitrogen compounds, TRANS., 1069.
 — refractive indices and magnetic rotations of sulphuric acid solutions, TRANS., 99.
 — the hydrate theory of solutions. Some compounds of the alkylamines and ammonia with water, TRANS., 141.
 — the hydrates of hydrogen chloride, PROC., 1893, 45.
 — the hydrates of sodium, potassium, and lithium hydroxide, TRANS., 890.
 Pickersgill, N. See Kehrman.
 Pictet, A., and E. Patry, phenanthridine, i, 722.
 Pictet, R., formation of nitro-derivatives at low temperatures, i, 460.
 — general method of chemical synthesis, ii, 112, 451.
 Pinkus, G., penthiazolines, i, 427.
 Pinkus, G. See also Gabriel.
 Pinner, A., action of hydrazine on imido-ethers, i, 710.
 — constitution of nicotine, i, 286, 443, 736.
 — pyrimidines free from oxygen, i, 735.
 Pinnow, J., action of benzenesulphonic chloride on amidoximes, i, 332.
 Pinnow, J., and G. Pistor, action of formaldehyde on nitrosodimethylaniline, i, 509.
 Pionchon, incomplete oxidation of aluminium, ii, 572.
 Pirsson, L. V., volcanic rocks from Gough's Island, S. Atlantic, ii, 539.
 Pisani, F., idocrase, ii, 578.
 Pistor, G. See Pinnow.
 Pitsch, O., are nitrates indispensable for the growth of plants? ii, 385.
 Plaats. See Van der Plaats.
 Placet, E., preparation of metallic chromium by electrolysis, ii, 122.
 Planta, A. v., and E. Schulze, estimation of stachyose in the tubers of *Stachys tuberosa*, ii, 53.
 — organic bases in the tubers of *Stachys tuberosa*: stachydrine, i, 447, 679.
 Plöchl, J. See Miller.
 Plugge, P. C., cerberin, i, 481.
 — volumetric estimation of alkaloids, ii, 199.
 Poirault, G. See Bertrand.
 Poleck, T., ethyl alcohol in oil of roses, ii, 181.
 — jalapin, i, 225.
 Poleck, T., and B. Grützner, crystalline alloy of iron and tungsten, ii, 170.
 Politis, G., asparagine as a nutritive substance, ii, 27.
 Pollard, W. See Hutchinson.
 Pomeranz, C., bergapten, i, 342.
 — new synthesis of isoquinoline, i, 607.
 Pomfret, H. W., physiological action of organic oximides, ii, 584.
 Pope, W. J. See Kipping.
 Posner, T., cinnamylamine and its derivatives, i, 568.
 Potilitzin, A., decomposition of strontium bromate by heat, ii, 11.
 — determination of the melting point of inorganic substances, ii, 314.
 Potilitzin, A. L., formation of super-saturated solutions, ii, 509.
 — structure of nitro-compounds and of the oxides of nitrogen, i, 636.
 Poulenc, C., anhydrous and crystalline iron fluorides, ii, 122.
 — chromium fluorides, ii, 281.
 — copper fluorides, ii, 525.
 — fluorides of the alkaline earths, ii, 414.
 — zinc and cadmium fluorides, ii, 321.
 Prausnitz, W., metabolism during inanition, ii, 477.
 — phloridzin diabetes, ii, 480.
 Prescott, A. B., mercuriodides of organic bases, i, 376.
 Preston, H. L., new meteorite from Kentucky, ii, 79.
 Pribram, R., and C. Glücksmann, behaviour of thiocarbonates towards phenols, i, 75.
 Priest, M. See Shenstone.
 Prinz, W., crystalline forms of chromium and iridium, ii, 281.
 Prior, estimation of acids in beer, ii, 53.
 Priwoznik, E., tellurium, ii, 205.
 Prost, E., and V. Hassreidter, Schaffner's volumetric zinc process, ii, 92.
 Prud'homme, direct conversion of aniline into nitrobenzene, i, 323.
 Prud'homme, M., relation between heats of formation and temperatures of reaction, ii, 152.
 Prud'homme and C. Rabaut, constitution of colouring matters of the rosaniline group, i, 640.
 — dihydroxyanthraquinone-formamide, i, 659.

- Pukall, W., clay filters, ii, 368.
 Pulvermacher, G., formaldehyde, i, 389.
 — phenyl- α -hydroxycrotonic acid, i, 342.
 Pum, G., molecular transformation of cinchonine, i, 181.
 Purdie, T., resolution of lactic acid into its optically active components, TRANS., 1143.
 Purdie, T., and W. Marshall, resolution of methoxysuccinic acid into its optically active components, TRANS., 217.
 Purdie, T., and J. W. Walker, optically active ethoxysuccinic acid, TRANS., 229.
 Purgotti, A., action of sodium sulphide on orthodiazophenol chloride, i, 330.
 — paranitrophenylhydrazine, i, 155.
 — reduction of benzilehydrazone, i, 354.
 Puschl, C., elasticity of gases, ii, 9.
 Psychlau, E. See Claus.

Q.

- Quantin, H., analysis of mixtures of ammonia and methylamines, ii, 104.

R.

- Rabaut, C. See Prud'homme.
 Ragozin, V., zinc isopropide, i, 622.
 Raissonnier, L., bye-products of the action of sodium hydroxide on glycerol, i, 246.
 Ramage, H. See Hartley.
 Ramsay, W., note on the combination of dry gases, PROC., 1893, 165.
 Ramsay, W., and Miss E. Aston, the atomic weight of boron, TRANS., 207.
 Ramsay, W., and J. Shields, the boiling point of nitrous oxide at atmospheric pressure and the melting point of solid nitrous oxide, TRANS., 833.
 — the molecular complexity of liquids, TRANS., 1089.
 Ramsden, proteids of white of egg, i, 379.
 Randall, W. W., double chlorides of lead and ammonium, ii, 523.
 Rau, A., estimation of succinic acid, ii, 557.
 — succinic acid, i, 10.
 Rave, P., and B. Tollens, lactone from formaldehyde and levulinic acid, i, 628.
 Rave, F., and B. Tollens, penterythritol, i, 617.
 Rayleigh, Lord, densities of the principal gases, ii, 514.
 — the relative densities of hydrogen and oxygen, ii, 10.
 Recklinghausen, M. v., mercurial thermometer for temperatures up to 550°, ii, 443.
 — phosphorus sulphides, ii, 458.
 Recoura, A., chromopyrosulphuric acid, ii, 528.
 — chromosulphuric, chromotrisulphuric, and chromosulphochromic acids, ii, 470.
 Reed, L., notes on capillary separation of substances in solution, PROC., 1893, 123.
 Reese, C. L., formation of phosphate nodules, ii, 77.
 Reformatsky, A. See Markovnikoff.
 Regelsberger, F., assay of aluminium and some of its alloys, ii, 48.
 Rehe, E. See Nietzki.
 Reiche, F. See Fränckel.
 Reid, E. W., mucin granules of *Myxine glutinosa*, ii, 429.
 Reinbrecht, O., lactosecarboxylic and maltosecarboxylic acids, i, 148.
 Reinhardt, H., analysis of aniline oils, ii, 605.
 Reis, M. A. v., estimation of manganese in iron, ii, 304.
 Reischle, A., new alkali borates, ii, 460.
 Reischle, A. K., estimation of boric acid, ii, 491.
 Reissert, A., di- γ -amidopropylacetic acid and octahydro-1:1-naphthopyridine, i, 687.
 — products of the action of aniline on dibromosuccinic acid, i, 564.
 Reissert, A. See also Junghahn.
 Reitmair, O., and A. Stutzer, estimation of nitrous acid in sodium nitrite, ii, 43.
 Remertz, J. See Harnack.
 Remmler, H., cobalt, ii, 211.
 Remmler, W. See Jannasch.
 Remsen, I., and P. J. Dashiell, decomposition of diazo-compounds, i, 325.
 Rennie, E. H., the colouring matters of *Drosera Whittakeri*, TRANS., 1083.
 Retgers, J. W., crystalline nature of red phosphorus, ii, 457.
 — determination of the specific gravity of salts soluble in water, ii, 363.
 — isomorphism, ii, 161.

- Retgers, J. W., solubility of mercuric iodide in diiodomethane, ii, 374.
 — solubility of metallic iodides, &c., in diiodomethane, ii, 378.
 — sublimation of arsenic, ii, 570.
 — use of thallium silver nitrate for separating minerals, ii, 294.
 Révay, G. See Perkin.
 Reverdin, F., and C. de la Harpe, action of acetic anhydride on dimethylaniline, i, 23.
 — amidonaphtholsulphonic acids, i, 478.
 — dinitrophenol, i, 19.
 — preparation of naphthidine, i, 421.
 Reyckler, A., diffusibility of certain gases through a caoutchouc membrane, ii, 564.
 — nature of solutions, ii, 315.
 — preparation of carbamide, i, 696.
 Rheindorff, T. See Wallach.
 Rhodin, S., experiments with ammonium sulphate and sodium nitrate for barley and oats, ii, 593.
 Riban, J., colorimetric estimation of iron, ii, 50.
 Richards, T. W., atomic weight of barium, ii, 463.
 — atomic weight of copper, ii, 12.
 Richardson, A., the action of light in preventing putrefactive decomposition, and in inducing the formation of hydrogen peroxide in organic liquids, TRANS., 1109.
 Richardson, F. W., estimation of silk in fabrics, ii, 611.
 Richarz, F., law of Dulong and Petit, ii, 404.
 Richet, C., toxicity of certain mineral salts, ii, 179.
 Richet, C. See also Hanriot.
 Richmond, H. D., estimation of total solids in milk, ii, 252.
 — Leffmann and Beam's method for the estimation of milk fat, ii, 308.
 — the Reichert process, ii, 307.
 Rideal, S., sulphuric acid hydrolysis of butter fat, ii, 602.
 Riedel, J. D., names of new remedies, i, 225.
 Rietschoten. See Van Rietschoten.
 Riggs, R. B., separation of magnesium chloride from the chlorides of sodium and potassium, ii, 46.
 Rijn Van Alkemade. See Van Rijn Van Alkemade.
 Rimbach, E., atomic weight of boron, ii, 207.
 — employment of borax for standardising acids, ii, 233.
 Ripper, M., estimation of sulphurous acid in wine, ii, 189.
 — gravimetric estimation of sulphuric acid, ii, 239.
 Ritter, A. See Cremer.
 Roberts, Miss C. F., estimation of chlorates and nitrates, and of nitrates and nitrites in one operation, ii, 596.
 — reduction of nitric acid by ferrous salts, ii, 595.
 Robertson, G. H., the Planté lead | sulphuric acid | lead peroxide cell from a chemical standpoint, ii, 3.
 Robertson, G. H. See also Armstrong.
 Robineau, F. and G. Rollin, detection of iodates in iodides, ii, 183.
 — volumetric estimation of acetone, ii, 556.
 Robinson, F. C., phosphoric acid in beryl, ii, 215.
 Röhmann, F., conversion of starch into sugar by means of blood serum, i, 187.
 — diastatic ferment in lymph, ii, 333.
 Rössing, A. See Otto.
 Röttger, H., qualitative and quantitative wax analysis, ii, 351.
 Rogers, W. A. C., the preparation of active amyl alcohol and active valeric acid from fusel oil, TRANS., 1130.
 Rogoff, M., volume changes in aqueous solutions, ii, 447.
 Rollin, G. See Robineau.
 Roloff, M., applications of Beckmann's boiling point method apparatus, ii, 260.
 Romig, E. See Schraube.
 Roozeboom, H. W. B., hydrates of ferric chloride, ii, 119.
 Rose, T. K., detection of gold in dilute solutions, ii, 245.
 — limits of accuracy attained in gold bullion assay, TRANS., 700.
 — the volatilisation of metallic gold, TRANS., 714.
 Rosenbach, O., chromic acid as a reagent for albumin: bile pigments in urine, ii, 200.
 Rosenbaum, M., estimation of chlorides, hypochlorites, and chlorates in presence of one another, ii, 388.
 Rosenberg, N., derivatives of the β -naphtholcarboxylic acid melting at 216° , i, 221.
 Rosenfeld, M., decomposition of aqueous vapour by magnesium, ii, 168.
 Rosenheim, A., action of inorganic and metallic oxides on organic acids, i, 626.
 — oxalic acid derivatives, i, 457.

- Rosenheim, A., and C. Friedheim, estimation of vanadic oxide, ii, 195.
- Rosenheim, O., and J. Tafel, oxidation of parahydroxyquinoline, i, 605.
- Rosenheim, T., occurrence of ammonia in the stomach contents, ii, 177.
- Rosenstiehl, A., acid salts and constitution of rosanilines, i, 332.
- Roser, W., constitution of the so-called quinoline ammonium bases, i, 177.
- Rosin, H., detection of bile pigments in urine, ii, 398.
- urinary colouring matters, i, 539.
- Rothenburg, R., v., action of hydrazine hydrate on organic halogen compounds, i, 410.
- benzo-3-phenylpyridazalone, i, 368.
- derivatives of pyrazolone, i, 729.
- pyrazolone, i, 180, 367, 428.
- pyrazolone from ethylic acetylenedicarboxylate, i, 611.
- pyrazolone from ethylic propiolate, i, 611.
- pyridazalone, i, 732.
- reaction of hydrazine hydrate with the nitro-, nitroso-, and isonitroso-groups, i, 701.
- Rouffaer, H. A., action of phthalic chloride on trinitraniline, i, 515.
- Rousseau, G., action of water vapour on ferric chloride, ii, 280.
- basicity and functions of manganous acid, ii, 416.
- cyclic condensation of carbon; artificial production of the diamond, ii, 519.
- Rousseau, G., and H. Allaire, bromoborates, ii, 518.
- iron chloroborate, and chloroborates isomorphous with boracite, ii, 468.
- Rouvier, G., combination of iodine with starch, i, 683.
- Rozycki, P., estimation of aluminium in steel, bronze, and ferroaluminium, ii, 243.
- Rubricius, H., estimation of silicon in pig iron, ii, 435.
- Rubtsoff, P., estimation of nitrogen in organic nitrates, ii, 184.
- oximidoacetic acid, i, 391.
- Rudert, P., action of phosphorus oxychloride and of phosphorus thiochloride on aromatic amines, i, 323.
- Rudevitch, W., a decanaphthene from Caucasian petroleum, i, 635.
- Rudnew, W., molecular compounds of amines, i, 128.
- Rücker, A. W., density and composition of sulphuric acid solutions, ii, 61.
- Rüdorff, F., quantitative analysis by electrolysis, ii, 93, 305, 391.
- Ruhemann, S., dihydroxypyridines, i, 527.
- formation of pyridine derivatives from unsaturated acids: dihydroxypyridines (continuation), TRANS., 874.
- the formation of pyridine derivatives from unsaturated acids: benzyl-dihydroxypyridine, TRANS., 259.
- Runge, C. See Kayser.
- Rupe, H., and C. Maull, camphoric acid derivatives, i, 524.
- Rusanoff, A., condensation of chloral hydrate with naphthols, i, 173.
- indoxazen-derivatives, i, 95.
- preparation of chloracetic acid, i, 131.
- Ruspaggiari, G. See Piccinini.
- Ryn. See Van Ryn.

S.

- Saake, W., glycogen, ii, 581.
- Sabanéeff, A., cryoscopy of albumose and peptone, i, 680.
- Sabanéeff, A., and I. Antushevitch, cryoscopy of caramel, i, 619.
- Sabatier, P., and J. B. Senderens, nitrocopper, ii, 374.
- Sachs, J., substitution products of the naphthyl ethers, i, 274.
- Sachs, J. See also Marchlewski.
- Sachse, H., explanation of affinity, ii, 266.
- Sachse, H. See also Liebermann.
- Sachsse, R., and A. Becker, behaviour of ferric oxide in soil and rocks, ii, 243.
- Saint Martin. See De Saint Martin.
- Saladin, electrical furnace, ii, 507.
- Salazar and Newmann, oxidation solutions of hydrogen sulphide, ii, 66.
- Salkowski, E., relation of the urinary carbohydrates to humous substances, ii, 82.
- pentoses in urine, ii, 100.
- synovin and mucin, ii, 330.
- Salomon, A., oxazolines and thioazolines, i, 532.
- Salomon, G., episarkine, ii, 542.
- formation of uric acid, ii, 428.
- occurrence of glycogen in blood, ii, 333.
- Saltar, J. C. See Smith.
- Salvatori, S., estimation of glycerol in wine and other fermented liquids, ii, 248.

- Salvatori, S., oxidation of glycerol in acid solution, ii, 247.
- Salzer, T., normal borax solution, ii, 294.
- Sanda, H. See Kiliani.
- Sanderval. See De Sanderval.
- Sandford, P. G., analysis of explosive nitro-compounds, ii, 196.
- Sani, G., essential oil of *Cochlearia armoracia*, i, 633.
- Sans. See Bertin-Sans.
- Sansoni, L., behaviour of hydrochloric acid to albumin in relation to the chemical investigation of gastric juice, i, 233.
- Saporta. See De Saporta.
- Sattler, E. See Wislicenus.
- Saul, E. See Meyer.
- Saunders, C. E., derivatives of pyromucamide, i, 313.
- Saytzeff, A., structure of oleic, erucic, and isomeric acids, i, 551.
- Saytzeff, M. C., and A. Saytzeff, action of sodium hydrogen sulphite and of sulphuric acid on oleic and erucic acids, i, 549.
- Saytzeff, N., allylmethylethylcarbinol, i, 544.
- transformation of brassidic acid into erucic and isoerucic acids, i, 550.
- Saytzeff, N. See also Alexandroff.
- Schacherl, G., estimation of phenol in crude carbolic acid, ii, 394.
- Schad, P., synthesis of ring compounds from benzene derivatives with open side chains, i, 279.
- Schäfer, J. See Muthmann.
- Schaffer, goats' milk and its detection in admixture with cows' milk, ii, 396.
- Schall, C., brazilin methyl ether, i, 225.
- molecular weight of the carbodimides, i, 701.
- Wessel's dicarbo-base from phenylhydrazine and carbodiphenylimide, i, 461.
- Scharizer, R., falkenhaynite, a new mineral of the wittichenite group, ii, 576.
- Scheibe, R., hauchecornite, a nickel bismuth sulphide, ii, 418.
- Scheibler, C., action of alkalis on betaïne, i, 498.
- Scheibler, C., and H. Mittelmeier, trehalum, a new carbohydrate, i, 496.
- Scheidt, M. See Magnanini.
- Scherer, F., arsenical pyrites, ii, 418.
- Schierbeck, N. P., influence of carbonic anhydride on the diastatic and peptone-forming ferments in the animal organism, ii, 475.
- Schiff, H., anilide of gallic acid, i, 167.
- Schiffer, A., non-crystallisable products of the action of diastase on starch, i, 127.
- Schindler, T., action of sulphuric acid on β -trimethylethylidenelactic acid, i, 71.
- Schindler, W., estimation of sulphur in iron, ii, 389.
- Schjerning, H., compounds of phenylhydrazine with metallic salts, i, 267.
- Schlagdenhauffen and Bloch, action of aqua regia on carbon bisulphide, ii, 571.
- Schliemann, J. See Lellmann.
- Schlömann, W., action of metaphosphoric acid on organic bases, i, 452.
- Schloosing, T., influence of the distribution of manures on the soil on their utilisation, ii, 141.
- Schloosing, T., jun., hygroscopic properties of textile fabrics, ii, 368.
- interchange of carbonic anhydride and oxygen between plants and the atmosphere, ii, 137, 180.
- Schloosing, T., jun., and E. Laurent, absorption of atmospheric nitrogen by plants, ii, 84, 138.
- — fixation of free nitrogen by plants, ii, 336.
- Schmid, E. See Nobbe.
- Schmid, F. See Lunge.
- Schmid, J., constitution of β -hydroxynaphthoic acid (m, p. 216°), i, 475.
- Schmidmer, E. See Fischer.
- Schmidt, A., minerals of the pyroxene group, ii, 130.
- Schmidt, A. See also Majert.
- Schmidt, E., constituents of Sumatragum benzoïn, i, 481.
- salts of caffeine, i, 489.
- Schmidt, E. and W. Gölich, codeïne, i, 675.
- Schmidt, E., G. Koenig, and W. Tietz, alkaloïds of the Papaveraceæ, i, 490.
- Schmidt, F. W., can arsenic be converted quantitatively into hydrogen arsenide? ii, 186.
- Schmidt, F. W. See also Krüss.
- Schmidt, G. C., action of nitric acid on potassium dichromate, ii, 16.
- periodic law, ii, 267.
- Schmidt, J. H., estimation of quinine in cinchona barks, ii, 310.
- Schmidt, M., and H. Dreyer, separation and estimation of tin, antimony, lead, and copper in alloys, ii, 95.
- Schmidt, R., alkyltoluidinesulphonic acids, i, 584.
- Schmitt, T. F., estimation of nitrogen in nitrates, ii, 434.
- Schmitz, C., putrefaction in the intestine, ii, 137.

- Schmitz, J. See Behrend.
- Schneegans, A., and J. E. Gerock, detection of free salicylic acid in salicylaldehyde and methylsalicylic acid, ii, 503.
- Schneider, E. A., a case of solid solution, ii, 73.
- behaviour of colloids in organic solvents at the critical temperature of the solvent, ii, 259.
- ferric phosphate, ii, 573.
- the variety of gold purple soluble in water, ii, 575.
- Schneider, E. A. See also Barus, Clarke.
- Schneider, L., estimation of phosphorus in steel, &c., ii, 392.
- Schnell, H. See Auwers.
- Schöller, M. See Claus.
- Schöneis, W., estimation of aluminium in steel, bronze, &c., ii, 49.
- Schönrock, O., magnetic rotation of liquids and salt solutions, ii, 442.
- Schöpf, M., constitution of the β -hydroxynaphthoic acid (m. p. 216°), i, 476.
- xanthone derivatives and orthocresotic anhydride, i, 217.
- Scholl, R., fulminic acid and its derivatives, i, 542.
- Schoor, W. K. J., anemonin and its occurrence, i, 727.
- Schorlemmer, C., obituary notice of, TRANS., 756.
- Schramm, J., action of aluminium chloride on chlorides and bromides of aromatic radicles, i, 561.
- cinnamene hydrochloride and hydrobromide, i, 563.
- Schranzhofer, F. See Goldschmidt.
- Schraube, C., and E. Romig, isoparatolylrosinduline, i, 339.
- Schrauf, A., metacinnabarite from Idria, ii, 418.
- Schreinemakers, F. A. H., cryohydric temperatures, ii, 512.
- double salts of lead and potassium iodides, ii, 118.
- graphical deductions from the solution isotherms of a double salt and its components, ii, 260.
- Schröder, I., dependence of the solubility of a solid on its melting point, ii, 366.
- Schröder, M., estimation of sugar in cocoa preparations, ii, 100.
- Schröder van der Kolk, J. L. C., mixed crystals of ammonium and ferric chlorides, ii, 280.
- Schroeder. See Stahl-Schroeder.
- Schröter, G., and M. Lewinski, action of thionyl chloride on alkylic carbamates, i, 696.
- Schröter, G. See also Michaelis.
- Schryver, S. B., researches on the oxidation products of turpentine oil, TRANS., 1327.
- Schüpphaus, R. C., alcohols in fusel oil, i, 63.
- Schützenberger, P., chemical constitution of peptones, i, 235.
- the volatilisation of silica, ii, 460.
- Schultess, O. See Michael.
- Schultz-Schultzenstein, C., influence of tea and coffee on artificial digestion, ii, 540.
- Schulze, E., carbohydrates in leguminous seeds, ii, 139.
- constitution of leucine, i, 195.
- nitrogenous constituents of the seedlings of *Vicia sativa*, ii, 85.
- Schulze, E., and S. Frankfurt, occurrence of betaine and choline in the sprouts of barley and wheat, i, 684.
- Schulze, E., and A. Likiernik, constitution of leucine, i, 309.
- Schulze, E. See also Planta.
- Schulze, H., cupro-iodargyrite, ii, 285.
- the thiocyanate test for iron, ii, 438.
- Schunck, E., chlorophyll, i, 41.
- Schunck, E., and L. Marchlewski, action of hydrogen peroxide on aniline, i, 197.
- phlorose, i, 384.
- supplementary notes on madder colouring matters, TRANS., 969.
- Schuster, A., and A. W. Crossley, electrolysis of silver nitrate in a vacuum, ii, 4.
- Schwalbe, C. See Melikoff.
- Schwalm, A. See Delisle.
- Schwechten, E. See Erdmann.
- Schweitzer, H. See Breyer.
- Scott, A., composition of water by volume, ii, 515.
- Seeberger, L. See Bamberger.
- Seegen, J., detection of small quantities of sugar in urine, ii, 349.
- formation of sugar in the liver, ii, 25.
- precipitation of proteids from blood preparatory to the estimation of sugar, ii, 398.
- Selch, E., diresorcinol, i, 352.
- Selivanoff, T., amides of hypoidous acid, i, 392.
- haloid substitution products of amides, i, 388.
- influence of negative groups in organic compounds, i, 381.
- mixed anhydrides of hypochlorous and analogous acids, i, 192, 305.

- Selivanoff, T., trichloromethane-sulphonic chloride, i, 458.
- Sell, W. J., and T. H. Easterfield, studies on citrazinic acid. Part I, TRANS., 1035.
- Semenoff, V., homologues of citraconic, itaconic, and mesaconic acids, i, 194.
- Semmler, F. W., camphors containing the group $\text{CO}\cdot\text{CH}_3$, i, 107.
- citronellaldehyde, i, 685.
- conversion of tanacetoxime into 1:3:4-cymidine, i, 78.
- derivatives of ketopentamethylene and ketoexamethylene, i, 129.
- derivatives of β -methyladipic acid, i, 396.
- essential oil of garlic (*Allium sativum*), i, 103.
- essential oil of onion (*Allium cepa*), i, 104.
- Senator, H. See Lehmann.
- Senderens, J. See Sabatier.
- Senderens, J. B., action of sulphur in presence of water on salts of polybasic acids, ii, 205.
- Sestini, F., experiments with wheat on the substitution of beryllium for magnesium, ii, 228.
- Seubert, K., and M. Elten, basic metallic sulphites, ii, 455.
- thallium sulphite, ii, 278.
- Severini, O., constitution of acetyl-1-phenylpyrazole, i, 179.
- pyrazole compounds, i, 671.
- Severini, O. See also Balbiano.
- Seyewetz, A. See Lumière.
- Seyler, C. A., supersaturation of solutions of oxygen in water, ii, 306.
- Seyler. See Hoppe-Seyler.
- Shaw, G. E., hexiodobenzene, i, 14.
- Shenstone, W. A., and C. R. Beck, note on the preparation of platinum chloride and on the interaction of chlorine and mercury, PROC., 1893, 38.
- preparing phosphoric anhydride free from the lower oxides of phosphorus, TRANS., 475.
- Shenstone, W. A., and M. Priest, studies on the formation of ozone from oxygen, TRANS., 938.
- Shepherd, W. F. J. See Dunstan.
- Shields, J., hydrolysis in aqueous salt solutions, ii, 448.
- the relative strengths or avidities of some compounds of weak acid character, PROC., 1893, 144.
- Shields, J. See Ramsay.
- Shimoyama, Y., a new unsaturated fatty acid, i, 189.
- Shimoyama, Y., and H. Ono, occurrence of thymol in the ethereal oil of *Mosula Japonica*, ii, 181.
- Shinn, O. L. See Smith.
- Shober, W. B., reaction of alcohols with paradiabzenzenesulphonic acid, i, 639.
- Shore, L. E., and M. C. Tebb, conversion of maltose into dextrose, ii, 23.
- Shutt, F. T., Babcock's method of milk analysis, ii, 251.
- Siebert, H. See Michaelis.
- Siegfeld, M. See Auwers.
- Sigmund, W., relations between fat-decomposing and glucoside-decomposing ferments, ii, 85.
- Silber, P. See Ciamician.
- Silva. See Ferreira de Silva.
- Simon, L., derivatives of pyruvic acid, i, 552.
- preparation of amylic pyruvate, i, 627.
- Simonini, A., action of iodine on the silver salts of fatty acids, i, 391.
- Sims, W. E. See Hartog.
- Singer, L. See Engler.
- Siringo, G. See Peratoner.
- Sjögren, H., adelite and svabite, new Swedish minerals, ii, 420.
- astochite, ii, 421.
- lāngbanite, ii, 421.
- Skinner, S. See Glazebrook.
- Skraup, Z. H., conversion of cinchona alkaloids into isomerides, i, 56.
- transformations of quinine, i, 737.
- Skraup, Z. H., and F. K. v. Norwall, new isomerides of the ethioides of the cinchona alkaloids, i, 738.
- Smetham, A., rapid saponification of oils, ii, 603.
- Smett, A. See Petterson.
- Smith, A., condensation of acetone with benzoin by means of potassium cyanide, i, 219.
- condensations with potassium cyanide, i, 219.
- Smith, E. F., action of molybdenum and tungsten on solutions of silver, gold, and other metals, ii, 170.
- electrolytic separation of platinum and palladium from iridium, ii, 97.
- Smith, E. F., and H. L. Dieck, a crystalline chromium tungstate, ii, 574.
- Smith, E. F., and V. Lenher, action of gaseous ammonia on molybdenyl chloride, ii, 529.
- Smith, E. F., and J. B. Moyer, electrolytic separations, ii, 496.
- electrolytical separation of mercury from bismuth, ii, 496.
- Smith, E. F., and V. Oberholtzer, action of gases on molybdenum and tungsten, ii, 574.

- Smith, E. F., and V. Oberholtzer, action of hydrogen haloids on molybdic acid, ii, 471.
- Smith, E. F., and J. C. Saltar, electrolytic separation of metals, ii, 495.
- Smith, E. F., and O. L. Shinn, action of gaseous ammonia on tungstyl chloride, ii, 531.
- Smith, E. F., and D. L. Wallace, electrolytic separation of copper from antimony, ii, 495.
- Smith, E. F. See also Keller, Lorimer.
- Smith, F., dandruff of the horse, ii, 585.
- Smith, J. L. See Haldane.
- Smith, W. J., influence of certain sulphur compounds on metabolism, ii, 288.
- physiological action of the isomeric ethylic thiocarbamates, ii, 584.
- Smith, W. S., optical isomerides of *d*-mannoheptonic acid, *d*-mannoheptose, and perseitol, i, 147.
- Smoluchowski, T. v. See Herzig.
- Smyth, C. H., jun., the Clinton iron ore, ii, 76.
- Snow, B. W., infra-red emission spectrum of the alkalis, ii, 58.
- Söderbaum, H. G., behaviour of certain aromatic isonitrosoketones towards acetic anhydride and acetic chloride, i, 159.
- Söderbaum, H. G., and O. Widman, preparation of orthonitrobenzyl alcohol, i, 74.
- Söderbaum, H. G. See also Abenius.
- Sokoloff, N. V., estimation of theïne in tea, ii, 352.
- Solaro, A., estimation of chlorine in wine, ii, 233.
- Soldaini, A., alkaloids of the seeds of *Lupinus albus*, i, 379.
- the deliquescent alkaloid from *Lupinus albus*, i, 739.
- Sorel, E., distillation of mixtures of alcohol and water, ii, 347.
- Speransky, A., electrical conductivity and freezing point of aqueous solutions of fluorine compounds, ii, 315.
- velocity of sugar inversion in presence of acetic and lactic acids, ii, 112.
- Spiegel, L., action of phenylhydrazine on cantharidin, i, 40, 278.
- gelseminine, i, 492.
- Spiegler, E., detection of albumin in urine, ii, 399.
- Spilker, A., indene and hydrindene, i, 518.
- Spindler, E., action of hydriodic acid on piperidine, i, 174.
- heptanaphthene from Caucasian naphtha, i, 151.
- Spitz, G. See Hönig.
- Spitzer, W., use of certain colouring matters for the determination of affinities, ii, 64.
- Spizzichino, E., essence of *Eucalyptus globulus*, i, 726.
- Sponholz, E., volumetric estimation of thallium, ii, 93.
- Sponholz, K., and E. Sponholz, precipitation of alumina in presence of lithium, ii, 95.
- Spring, W., possibility of the existence of certain metals in the gaseous condition at temperatures below their fusing points, ii, 168.
- Spring, W., and M. Lucion, dehydration of copper hydroxide and certain of its basic salts in the presence of water, ii, 210.
- Staats, G., influence of frictional electricity on the formation of amalgams, ii, 441.
- Stahl-Schroeder, M., reversion of soluble calcium phosphate in soil, ii, 431.
- Stange, A. See Friedlaender.
- Stapelberg, E. See Claus.
- Starling, E. H., lymph secretion, ii, 219.
- Starr, J. E. See Ludeking.
- Stavenhagen, A., compounds of arsenious and sulphuric anhydrides, ii, 459.
- Stebbins, J. H., jun., action of sulphuric acid on quinol, i, 37.
- Stelzner, A. W., franckeite, a new ore from Bolivia, ii, 576.
- Stern, J., toxicological reactions: oils of pimento and cloves, ii, 397.
- Sternitzki, H. See Bamberger.
- Steude, M. See Engler.
- Stieglitz, J. See Lengfeld.
- Stift, A. See Strohmmer.
- Stock, A., auramines, i, 472.
- Stock, F. K., Stock's process for the estimation of nitrogen, ii, 297.
- Stockhausen, F., and L. Gattermann, aluminium chloride and nitro-compounds, i, 161.
- aromatic ketones, i, 163.
- Stockman, R., iron in chlorosis, ii, 427.
- physiological action of quinoline, isoquinoline, and their derivatives, ii, 585.
- Stoehr, C., piperidine bases of the β -series, i, 602.
- pyrazines, i, 486, 612, 675.

- Stoechr, C., pyrazines and piperazines, i, 486, 675.
- Stoechr, C., and M. Wagner, methyl-dipyridyls, i, 612.
- Stoechr, C. See also Jacobi.
- Stohmann, F., heat of combustion of organic compounds, ii, 59.
- Stohmann, F., and H. Langbein, thermochemistry of isomeric allyl and propenyl derivatives, ii, 153.
- Stohr, F. See Claus.
- Stokes, A. W., estimation of fat in milk by Babcock's method, ii, 251.
- Stokes, H. N., action of phosphorus oxychloride on aromatic silicates, i, 74.
- amidophosphoric acid, i, 315.
- benzylic silicate, i, 74.
- catalytic action of aluminium chloride on ethereal silicates, i, 62.
- Stoklasa, J., estimation of nitrogen in nitrates and in nitric acid, ii, 389.
- monomagnesium phosphate, ii, 168, 277.
- soluble phosphoric acid in superphosphate, ii, 549.
- Stolle, E., volumetric estimation of sulphuric acid in sulphates, ii, 188.
- Stone, G. C., separation of calcium and magnesium from zinc as phosphates, ii, 344.
- Stone, W. E., recent investigations on carbohydrates, i, 547.
- synthesis of sugars, i, 125.
- Stone, W. E., and W. H. Test, xylose, i, 294.
- Storbeck, O. See Michaelis.
- Storch, L., reduction of ferric salts and solution of ignited ferric oxide, ii, 468.
- Storch, L. See also Bamberger.
- Stracciati. See Bartoli.
- Strache, H., and S. Iritzer, oxidation of acid hydrazides by Fehling's solution, i, 331.
- Strache, H. See also Benedikt.
- Strassmann, F., nutritive value and elimination of alcohol, ii, 24.
- Streatfeild, F. W. See Meldola.
- Ström, T., action of sodium ethoxide and ammonia on isocapro lactone, i, 690.
- Strohmer, F., and A. Stift, composition and nutritive value of the tubers of *Stachys tuberosa*, ii, 225.
- Struve, H., chemico-legal examination of suspected blood stains, ii, 312.
- Stschukareff, A., valency of the dextro-terpenes in Russian turpentine, i, 358.
- Stutzer, A., estimation of the nitrogenous constituents of commercial peptone, ii, 146.
- Stutzer, A. See also Reitmaier.
- Sudborough, J. J. See Tilden.
- Süss, P., estimation of theobromine in cacao beans, ii, 198.
- Süßern, C. See Erdmann.
- Šule, O. See Pařížek.
- Sundwik, E. E., pnylostearyl alcohol, i, 125.
- Supino, R., estimation of acetone in urine, ii, 250.
- Sysoyeff, gas-volumetric analysis of nickel, ii, 393.
- Székely, S. See Liebermann.
- Szuhay, J., iodide of nitrogen, ii, 568.

T.

- Täuber, E., nitrohydroxyazo- and nitramidoazo-compounds, i, 570.
- orthodiamidodiphenyls, i, 96, 588.
- Tafel, J., oxidation of strychnine, i, 287.
- Tafel, J., and I. Vogel, action of carbamide on nitrosamines, i, 265.
- Tafel, J. See also Farchy, Rosenheim.
- Tahara, Y. See Einhorn.
- Talantzeff, Z., behenic acid, i, 548.
- Talbot, H. P., index to the literature of angelic and tiglic acids, i, 10.
- Talbot, H. P., and H. R. Moody, hydrogen peroxide solutions, ii, 369.
- Tammann, G., internal pressure in solutions, ii, 447.
- Tanatar, S., action of water on bromosuccinic acid, 192.
- heat of hydration of maleic anhydride, ii, 108.
- iodine monochloride, ii, 514.
- isomerism of fumaric and maleic acids, i, 193.
- thermochemical data for some organic acids, ii, 108.
- thermochemistry of chloracetic acid, i, 624.
- thermochemistry of α -dibromopropionic acid, ii, 358.
- thermochemistry of β -dibromopropionic acid, i, 625.
- Tanatar, S., and C. Tchelebieff, specific gravity of some isomeric acids, i, 11.
- Tanret, C., carbohydrates of the Jerusalem artichoke, i, 617.
- inulin, pseudoinulin, and inulinin, i, 385.
- Tappeiner, H. See Brandl.
- Tarible, combination of boron bromide with phosphorus tribromide, ii, 518.
- Tassinari, G., constitution of the dihydroxythiobenzenes, i, 461.

- Tate, A. N., obituary notice of, *TRANS.*, 764.
- Tate, G., the fermentation of dextrose, rhamnose, and mannitol by a lavo-lactic ferment, *TRANS.*, 1263.
- Taylor, T., obituary notice of, *TRANS.*, 765.
- Tchelebieff, C. See Tanatar.
- Tcherniac, J., preparation and properties of methyloxythiazole, i, 228.
- thiocyanacetone, i, 188.
- Tebb, M. C. See Shore.
- Teclu, N., determination of the intensity of rays, ii, 401.
- laboratory burner, ii, 368.
- Teed, F. L., detection and estimation of minute quantities of lead in the presence of copper and iron, ii, 242.
- Teichmann, H., preparation of benzidine sulphate, i, 469.
- Terreil, A., preparation of acicular basic zinc nitrate, ii, 209.
- Test, W. H. See Stone.
- Thiel, W., derivatives of campholenic acid, i, 423.
- Thiele, E., estimation of the vapour density of iodine in different atmospheres, ii, 154.
- Thiele, J., action of ammonia on hypochlorites, ii, 317.
- nitrosoguanidine, i, 389.
- Thiele, J., and J. T. Marais, tetrazole-derivatives from diazotetrazotic acid, i, 440.
- Thieme, B., salts and derivatives of phenylhydrazine, i, 154.
- Thilo, J., freezing points of sulphuric acid of different concentrations, ii, 262.
- Thörner, W., estimation of fat in milk, ii, 101.
- estimation of fibre in foods by means of the centrifugal apparatus, ii, 611.
- estimation of lactic acid in milk, ii, 250.
- Thomas, G. L. See Young.
- Thomas-Mamert, R., oxamidomaleamide and oxysuccinamide, i, 632.
- Thompson, W. H., the work of the kidney, ii, 542.
- Thomson, J. J., electrolysis of steam, ii, 515.
- Thorion, H. See Guérin.
- Thorp, F. H., action of hydroxylamine on orthobenzoylbenzoic acid, i, 466, 589.
- Thorpe, T. E., Kopp Memorial Lecture.—The life work of Herman Kopp, *TRANS.*, 775.
- the determination of the thermal expansion of liquids, *TRANS.*, 262.
- Thorpe, T. E., and L. M. Jones, the thermal expansion and specific volumes of certain paraffins and paraffin derivatives, *TRANS.*, 273.
- Threlfall, R., preparation of pure nitrogen, and attempts to condense it, ii, 270.
- Thugutt, S. J., deviations from the gaseous laws in solutions, ii, 265.
- mineral chemical studies, ii, 421.
- Tidy, C. M., obituary notice of, *TRANS.*, 766.
- Tietz, W. See Schmidt.
- Tigerstedt, A., action of alcoholic potash on the anilides, &c., of α -bromopropionic, -butyric, and -isobutyric acids, i, 51.
- simplification of the process of fractional distillation, ii, 204.
- Tilden, W. A., and M. O. Forster, the combination of hydrocarbons with picric acid and other nitro-compounds, *TRANS.*, 1388.
- Tilden, W. A., and J. H. Millar, formation and nitration of phenyldiazoimide, *TRANS.*, 256.
- Tilden, W. A., and J. J. Sudborough, action of nitrosyl chloride and of nitric peroxide on some members of the series of olefines, *TRANS.*, 479.
- Tilden, W. A., and S. Williamson, on the hydrocarbons derived from dipentene dihydrochloride, *TRANS.*, 292.
- Tinsley, J. D., analyses of kale, turnip salad, and okra, ii, 293.
- Tissier, L., fourth primary amyl alcohol, i, 542.
- normal amyl alcohol, i, 542.
- Tissot, G. See Michael.
- Tivoli, D., phenylamlecyanamide and β -diphenylsemithiocarbazine, i, 206.
- Töhl, A., and E. Bauch, di-iodometaxylene obtained from iodometaxylene and sulphuric acid, i, 407.
- Töhl, A., and R. Eckel, reactions of iodomesitylene, i, 407.
- Töhl, A., and A. Müller, behaviour of halogen derivatives of pseudocumene towards sulphuric acid, i, 408.
- Toepler, M., specific volume of sulphur, ii, 8.
- Tollens, B., birotation of glucose, i, 545.
- Tollens, B. See also Flint, Moschatos, Rave, Wissell.
- Tolotchko, action of sulphuric acid on menthol, i, 422.
- Torrey, J., estimation of sulphur in slags, ii, 89.
- Trapesonjanz, C., derivatives of

- propylenediamine and pseudobutyl-
enediamine, i, 79.
- Trapesonanzjan, C., ketoximes, i, 499.
- molecular refraction of compounds
containing nitrogen (aldoximes, ket-
oximes), ii, 401.
- Trapesonanzjan, C. See also Bis-
chhof.
- Trapp, J., ethereal oil of the seeds of
Cicuta virosa, i, 634.
- Traube, J., electrolytic dissociation
and ionisation, ii, 4.
- molecular volumes of dissolved
alkali salts and their relation to the
atomic volumes of the elements,
ii, 264.
- Traube, M., constitution of hydrogen
peroxide and of ozone, ii, 413.
- production of hydrogen peroxide
by spontaneous oxidation of zinc:
combustion in oxygen, ii, 412.
- sulphuryl peroxide (holoxide),
ii, 413.
- Traube, W., amide and imide of sulph-
uric acid, ii, 268.
- Travers, M. W., a method for the
preparation of acetylene, *Proc.*, 1893,
15.
- Trench, C. C. See Hodgkinson.
- Trevor, J. E., dissociation measure-
ments of feebly dissociated acids,
ii, 62.
- Trey, H., hydrogen sulphide apparatus,
ii, 268.
- Trillat, A., detection and estimation
of formaldehyde, ii, 439.
- new series of colouring matters,
i, 573.
- Trillat, A. See Jean.
- Trimble, H., chestnut bark tannin,
i, 343.
- Tripier, J., preparation of normal
caproic and hexylic acids, i, 687.
- Tristan, J. F. See Michaud.
- Troeger, J., action of hydrogen
chloride and hydrogen bromide on
liquid α -dichlorethyl cyanide, i, 121.
- metaldehyde and paraldehyde, i, 64.
- Tröger, J. See Otto.
- Troost, L., extraction of zirconium
and thorium oxides, ii, 532.
- preparation of zirconium and
thorium, ii, 473.
- Tsakoni, A. See Kablukoff.
- Tschaplowitz, F., estimation of clay
and sand in soils, ii, 97.
- Tschermak, G., and E. Ludwig, the
chlorite group, ii, 19.
- Tschirsch, trichosanthin and thallo-
chlore, i, 42.
- Tsuruta, K., heat of vaporisation of
hydrogen chloride, ii, 445.

- Tucker, G. P. See H. Pemberton.
- Turin, V., influence of gravity on con-
centration of solutions, ii, 315.
- Tust, K., and L. Gattermann,
action of phenol ethers on thiocarb-
imides, i, 154.
- Tutton, A. E., connection between the
atomic weight of contained metals
and the magnitude of the angles of
crystals of isomorphous series. A
study of the potassium, rubidium,
and caesium salts of the monoclinic
series of double sulphates,
 $R_2M(SO_4)_2 \cdot 6H_2O$, *Trans.*, 337.

U.

- Ullmann, localisation of mercury in
the animal organism, ii, 217.
- Ulseh, K., estimation of nitrogen in
nitrates, ii, 42.
- Ushinsky, poisoning by hydrogen
sulphide, ii, 83.
- Uspensky, N. N., action of phos-
phorus pentachloride on azoazoxy-
benzoic acids, i, 165.
- azoxybenzoic acids, i, 164.

V.

- Van Alkemade. See Van Rijn
van Alkemade.
- Van Bemmelen, J. M., and E. A.
Klobbie, amorphous hydrated ferric
oxide, crystalline ferric hydroxide,
potassium and sodium ferrites, ii, 169.
- Van der Heide, J. K., potassium
astrachanite, ii, 276.
- Vander Kolk. See Schröder van
der Kolk.
- Van der Plaatz, J. D., the atomic
weights of Stas, ii, 451.
- Van Deventer, C. M., a reaction of
nitrites and its applications: gaso-
metric estimation of nitrites by Schäf-
fer's reaction, ii, 298, 344.
- preparation of nitric oxide, ii, 271.
- Van Deventer, C. M., and B. H.
Jürgens, investigation of potable
water by Schäffer's nitrite reaction,
ii, 346.
- Van Dorp, W. A. See Hoogewerff.
- Van Eijk. See Cannepin.
- Van Leeuwen, J. D., influence of the
sulphur contained in coal-gas on the
estimation of sulphur by fusion,
ii, 239.
- Van Linge, A. R. See Buisman.
- Van Pesch, F. J., manufacture and
impurities of linseed cake, ii, 39.

- Van Rietschoten, W. H. See Goldschmidt.
- Van Rijn van Alkemade, A. C., graphical treatment of some thermodynamical problems on conditions of equilibrium in salt solutions with solid phases, ii, 363.
- Van Ryn, J. J. L., carpaïne, the alkaloid of the leaves of *Carica papaya*, i, 740.
- Van Wisselingh, C., cork and suberin, ii, 181.
- Varet, R., action of piperidine and pyridine on haloïd salts of cadmium, i, 43.
- action of piperidine on haloïd salts of mercury, i, 174.
- combination of quinoline with silver haloïds, i, 279.
- Vaubel, W., action of nascent bromine on some benzene derivatives, i, 560.
- assay of alkylanilines, ii, 605.
- Vedrödi, V., analysis of tobacco, ii, 504.
- Veley, V. H., conditions of the formation and decomposition of nitrous acid, ii, 413.
- the inertness of quicklime, TRANS., 821.
- Vernon, H. M., reactions of ferric salts with thiocyanates, i, 122, 290.
- Vèzes, M., an acid potassium platonitrite, ii, 213.
- electrometric study of potassium hydrogen triplatohexanitrite, ii, 256.
- Vèzes, M. See also Joly.
- Viefhaus, A., propylideneacetic acid and ethylidenepropionic acid, i, 392.
- Vignon, L., absorption of mercuric chloride from dilute solutions by cotton, i, 387.
- estimation of mercury in dilute solutions of mercuric chloride, ii, 345.
- preparation and properties of fibroïn, i, 183.
- rotatory power of fibroïn, i, 60.
- thermochemistry of carbon compounds of mixed function, ii, 6.
- Villavecchia, V., and G. Fabris, Baudoin's test for sesame oil, ii, 197.
- Villiers, A., and F. Borg, action of zinc and magnesium on solutions of metallic salts: estimation of potassium, ii, 521.
- estimation of phosphoric acid, ii, 434.
- Villiger, V. See Baeyer.
- Vines, S. H., and J. R. Green, reserve proteïd of the asparagus root, ii, 431.
- Violle, J. See Moissan.
- Vis, G. N., constitution of morphine, i, 536.
- isomerides and congeners of "analgen": ethoxy-4-benzoylamidoquinoline, i, 606.
- Visser. See De Visser.
- Vitali, D., absorption and physiological action of arsenic trisulphide, ii, 583.
- action of hydrogen arsenide, antimonide, and phosphide on silver nitrate, ii, 206.
- the transformations of arsenious anhydride in the organism, ii, 583.
- volumetric estimation of sulphates in potable waters, ii, 245.
- volumetric estimation of the alkaloïds and of some metals, ii, 606.
- Vizern, analysis of hydrogen alkali carbonates, ii, 190.
- Vogel, I. See Tafel.
- Vogel, J. H., estimation of sugar and tannin in wine, ii, 52.
- Vogel, O., the oxy-coal-gas flame for spectrum analysis, ii, 594.
- Voit, F., behaviour of galactose in a diabetic, ii, 177.
- metabolism in *diabetes mellitus*, ii, 177.
- secretion and absorption in the small intestine, ii, 582.
- Voit, K., nutritive value of asparagine, ii, 177.
- Volk, C. See Krüss.
- Volpi, A., a new acridine and an acridylpropionic acid, i, 350.
- Volpjan, L., preparation of optically inactive cymene from oil of caraway, i, 17.
- Voorhees, C. G. See Osborne.

W.

- Wachter, W., orthiodobenzoic acid and its derivatives, i, 577.
- Wagner, J., estimation of free acids in the presence of acid phosphates, i, 41.
- Wagner, M. See Stoehr.
- Wagstaffe, E. See Koenigs.
- Wahl, W. H. See Greene.
- Wakeman, A. J., behaviour of electrolytes in mixed solvents, ii, 257.
- Walbaum, H. See Bertram.
- Walden, P., affinity of organic acids, ii, 157.
- alleged optical activity of chlorofumaric acid: an active chlorosuccinic acid, i, 250.
- diffusion phenomena with precipitate membranes, ii, 203.
- Walden, P. See also Biscoff.
- Walfisz, B., action of hydriodic acid on carbon tetrachloride, i, 1.
- Walker, C., condensation products of

- the hydrazides of ethylic acetoacetate and oxalacetate, i, 367.
- Walker, C. H. H., products of the action of nitric acid on tin, *TRANS.*, 845.
- Walker, J., action of alcohols on lactones and alkyl salts, i, 500.
- the electrolysis of sodium orthoethylic camphorate, *TRANS.*, 495.
- the boiling points of homologous compounds. Part I. Simple and mixed ethers, *PROC.*, 1893, 145.
- Walker, J. See also Brown.
- Walker, J. W. See Purdie.
- Walker, W. See Wallach.
- Wallace, D. L. See Smith.
- Wallach, O., bases from polei oil, i, 115.
- constituents of oil of thuja, i, 105.
- oxidation of terpene derivatives, i, 596.
- Wallach, O., and A. Binz, optical rotatory power of certain compounds of the fenchylamine and menthylamine series, i, 725.
- Wallach, O., and F. Kerkhoff, terpineol, i, 595.
- Wallach, O., and M. Kuthe, isomeric menthylamines, i, 724.
- menthylamine, i, 105.
- Wallach, O., H. Kruse, and F. Kerkhoff, dihydrocarveol, i, 595.
- Wallach, O., and T. Rheindorff, ethereal oil of paracoto bark, i, 103.
- terpenes from resins, i, 100.
- Wallach, O., and W. Walker, sesquiterpenes, i, 101.
- Walter, G. See Baumann.
- Walter, J., ethylic orthoformates, i, 686.
- Wander, C. A. See Graebe.
- Warrington, R., detection and estimation of lead in tartaric and citric acids, ii, 599.
- Warmington, E., phenyluracil and its analogues, i, 369.
- Warren, H. N., action of silicon on gold, silver, platinum, and mercury, ii, 474.
- artificial production of mineral sulphides, ii, 214.
- combination of oxygen and hydrogen, ii, 410.
- decomposition of tin slags by the fluoride method, ii, 305.
- manufacture of borax, ii, 460.
- preparation of silicon and aluminium chlorides, ii, 11.
- refining gold, silver, and platinum, ii, 17.
- silicon, ii, 372.
- Warwick, H. S., electrolysis of metallic formates, ii, 191.
- Watson, G., preparation of phosphoric acid, ii, 272.
- Wavelet, C., volumetric estimation of phosphates, ii, 597.
- Wdowiszewski, H., estimation of phosphorus in steel, ii, 43.
- Wedel, R., titaniferous iron ore from the Breitfirst, ii, 382.
- Wedemeyer, K., estimation of nitrates by Schmitt's method, ii, 551.
- Wedemeyer, K. See also Arnold.
- Wegscheider, R., methylation of opianic acid, i, 167.
- Wehmer, C., formation of citric acid by the fermentation of glucose, ii, 591.
- Weibull, M., estimation of fat in bread, ii, 197.
- Weidel, H., and J. Hoff, non-nitrogenous acids derived from pyridine-carboxylic acids, i, 114.
- Weidel, H., and E. Hoppe, mesitylic acid and mesitonic acid, i, 72.
- Weigle, A., spectrophotometric investigation of the salts of aromatic bases, i, 333.
- Weinberg, A., paramidoalkylorthotoluidines, i, 265.
- Weinig, M., gravimetric estimation of sulphuric acid, ii, 145.
- Weinschenk, E. See Cohen, Kunz.
- Weisberg, J., effect of boiling with water on cane-sugar and raffinose, i, 64.
- Weiske, H., influence of increased or diminished consumption of food and of the salts added to the food on digestion and resorption, ii, 132.
- Weiss, estimation of fat in milk, ii, 396, 601.
- Weiss, F., phenylic hippurate and its condensation products, i, 579.
- Weissgerber, R. See Knoevenagel.
- Wells, H. L., cesium and potassium lead haloïds, ii, 322.
- cesium mercury haloïds, ii, 68.
- double salts of lead tetrachloride, ii, 523.
- halogen compounds of potassium and lead, ii, 524.
- quantitative separation of cesium and the preparation of pure cesium and rubidium compounds, ii, 521.
- rubidium lead haloïds, ii, 524.
- Wells, H. L., and W. R. Johnston, ammonium lead haloïds, ii, 523.
- Wells, H. L., and S. L. Penfield, herderite from Hebron, Maine, ii, 76.

- Wells, H. L., and H. L. Wheeler, cesium and rubidium aurochlorides and aurobromides, ii, 68.
- — — double haloids of silver and the alkali metals, ii, 69.
- — — pentahaloids of the alkali metals, ii, 68.
- — — rubidium and potassium trihaloids, ii, 67.
- Wendelstadt, H., and L. Bleibtreu, the volume and amount of proteid in single red blood corpuscles, ii, 332.
- Wendt, G., methylnaphthalenes, i, 171.
- Wenger, W. H., solubility of cream of tartar in dilute alcohol, i, 308.
- Wense, W., estimation of potassium as perchlorate, ii, 46, 190.
- Wense, W. See also Naupert.
- Werner, A., constitution of inorganic compounds, ii, 379.
- hydroxylamineacetic acid and its derivatives, i, 501.
- stereoisomerism of the benzhydroxamic acids, i, 510.
- Werner, A., and A. Miolati, constitution of metalamine salts, ii, 507.
- Werner, A. See also Hantzsch.
- Werth, J., origin of the diamond, ii, 285.
- Wheeler, H. L., cesium and rubidium iodates, ii, 68.
- double halogen compounds of arsenic with cesium and rubidium: compounds of arsenic trioxide with cesium, rubidium, and potassium haloids, ii, 572.
- double halogen compounds of tellurium with potassium, rubidium, and cesium, ii, 457.
- Wheeler, H. L. See also Wells.
- Wheelwright, E. See Bamberger.
- White, J. See Orndorff.
- Whitlock, T. C. See Dunnington.
- Widman, O., formation of dihydroquinazolines, i, 438.
- new method of preparing unsymmetrical derivatives of phenylhydrazine, i, 411.
- Widman, O. See also Söderbaum.
- Wiechmann, F. G., estimation of a mixture of saccharose, dextrose, and lævulose, ii, 99.
- estimation of iron and aluminium in bone-black, ii, 498.
- Wiedeburg, O., theory of diffusion, ii, 109.
- Wiederhold, E., solubility of resin oil, mineral oils, and mixtures thereof in acetone, ii, 350.
- Wiernik, J., and S. Wiernik, analysis of crude salt and brines, ii, 391.
- Wiernik, J. See also Marchal.
- Wijs, J. J. A., electrolytic dissociation of water, ii, 364.
- Wilde, H., spectrum of thallium, ii, 525.
- Wildermann, M., cyclical equilibria, ii, 367.
- non-electrolytic dissociation in solutions, ii, 509.
- Wiley, H. W. See Ewell.
- Willgerodt, C., aromatic iodochlorides, i, 149, 256.
- chlor- and brom-iodoso- and iodoxy-derivatives of benzene, i, 696.
- iodosobenzene and iodoxybenzene, i, 149.
- iodoso- and iodoxy-compounds, i, 256, 505, 561.
- orthochloriodosobenzene and orthochloriodoxybenzene, i, 506.
- Williamson, S. See Tilden.
- Willstätter, R. See Einhorn.
- Wilm, T., gold crystals containing mercury, ii, 534.
- occurrence of gold containing palladium in the Caucasus, ii, 475.
- rhodium salts, ii, 213.
- sodium platinocyanide, i, 541.
- Wilson, A. See Macfarlane.
- Wilson, F. R. L. See Hughes.
- Wilson, J. A., estimation of water and free fatty matter in soap, ii, 198.
- Winder, G. R. See Mason.
- Winkler, C., artificial minerals obtained in chemical industries, ii, 576.
- atomic weights of nickel and cobalt, ii, 469, 574.
- elementary nature of nickel and cobalt, ii, 469.
- Winogradsky, S., assimilation of atmospheric nitrogen by microbes, ii, 482.
- Winterstein, E., action of dilute alkalis and acids on cellulose, i, 127.
- inversion of some carbohydrates, i, 249.
- parent substance of wood-gum, i, 128.
- tunicin, i, 380, 497.
- vegetable amyloid, i, 127.
- Winton, A. L., modified Gunning-Kjeldahl method for use in presence of nitrates, ii, 145, 235.
- Wischin, C. See Morah.
- Wislicenus, J., brom-additive products of angelic and tiglic acids, i, 135, 455.
- Wislicenus, J., T. Kircheisen, and E. Sattler, condensation of chloral with ketones, i, 389.
- Wislicenus, J. See also Hentschel.

Wislicenus, W., action of benzaldehyde on ethylic oxalacetate, i, 714.
 — hydroxylamine, ii, 318.
 — synthesis of formazyl compounds by the action of diazobenzene on hydrazones, i, 156.
 Wislicenus, W., and A. Jensen, ethyl oxalacetate, i, 146.
 Wissell, L. v., and B. Tollens, furfuryl alcohol and its derivatives, i, 311.
 Wisselingsh. See Van Wisselingsh.
 Witkowski, A. See Olszewski.
 Witt, O. N., new laboratory apparatus, ii, 452.
 Witt, O. N., and E. S. Johnson, azo-derivatives of quinol, i, 571.
 Witt, O. N., and F. Mayer, azo-derivatives of catechol, i, 410.
 Witt, O. N., E. Noelting, and E. Grandmougin, indazole derivatives, i, 46.
 Witter, H. See Buchner.
 Wohl, A., action of phenylhydrazine on diazobenzene, i, 509.
 — dextrose, i, 292.
 — diazobenzene, i, 200.
 Wohl, A., and W. Marckwald, formula of glyoxaline, i, 438.
 Wolf, M. See Eckenroth.
 Wolff, C., quinazolines, i, 49.
 Wolff, E. v., and J. Eisenlohr, effect of salt on digestion, ii, 580.
 Wolff, L., constitution of dibromlevulinic acid, i, 689.
 — pyrazine, i, 373.
 — pyrazines and piperazines, i, 729.
 — synthesis of pyrazine, i, 612.
 Wolff, P. See Marckwald.
 Wolff, W., dinaphthoxanthene (methylenediphenylene oxide), i, 222.
 Woll, F. W., relative value of maize silage and field and fodder maize for milk and butter production, ii, 141.
 Woll, L. W. W., losses in ensiling and field-curing maize, ii, 141.
 Wrampelmeyer, E., amount of lecithin in butter, ii, 543.
 Wright, A. E., coagulation of blood, ii, 426.
 Wright, C. R. A., determination of specific gravity of liquids, ii, 264.
 — ternary alloys, ii, 15, 415, 522.
 Wulff, C., nucleïn bases, i, 309.
 — uric acid in the organism, ii, 384.
 Wynne, W. P. See Armstrong.
 Wyruboff, G., potassium tetrachromate and ammonium tetrachromate, ii, 528.
 — rotatory power of solutions, ii, 106.

Y.

Yeates, W. S., and E. F. Ayres, plattnerite from Idaho, ii, 75.
 Young, J. See Hodgkinson.
 Young, R. A., mucin in bone, ii, 134.
 Young, S., Van der Waals' "corresponding states," ii, 63.
 Young, S., and G. L. Thomas, the vapour pressures, molecular volumes, and critical constants of 10 of the lower esters, TRANS., 1191.
 Young, S. W. See Orndorff.
 Young, W. G., source of error in the volumetric estimation of chlorides by Mohr's methods, ii, 433.

Z.

Zacconi, A. See Kablukoff.
 Zahn, G. H., changes at the boundary between solutions of different concentration during the passage of an electric current, ii, 404.
 Zahorsky, B., calcium oxychloride, ii, 276.
 Zahorsky, B. See also Classen.
 Zakrzewski, J. v., specific gravity of ice, ii, 7.
 Zalonecki, R., acids occurring in petroleum, i, 268.
 Zanetti, C. U., constitution of the methylpyrrolines, i, 226.
 — conversion of carbazole into indole, i, 717.
 — products of the reduction of orthophenylenediacetonitrile, i, 267.
 Zanetti, C. U. See also Ciamician.
 Zecchini, F., atomic refractions of the elements with respect to sodium light, ii, 253.
 — molecular weight of metaldehyde, i, 301.
 — refraction constants of phosphorus in the free state and in its compounds with elements or monovalent groups, ii, 353.
 — refraction constants of the acids of phosphorus and their sodium salts, ii, 354.
 Zehnter, R. See Nietzki.
 Zelinsky, N., electrolytic conductivity of stereoisomeric acids, ii, 152.
 Zelinsky, N., and S. Krapivin, pinacone from ethyl methyl ketone, i, 390.
 Zernitschensky, P., palygorskite, ii, 174.
 Zenoni, M., condensation products of dimethylresorcinol and methylresorcinol with the nitrobenzaldehydes, i, 216.

- Zettel, T., cyanogen, i, 541.
- Ziegler, A., analysis of ferrochrome, ferroaluminium, ferrotungsten, ferrosilicon, and ferrotitanium, ii, 96.
- Zimmermann, R., estimation of phosphorus in steel and cast iron, ii, 44.
- Zincke, T., action of bleaching powder and of hypochlorous acid on quinones, i, 220.
- action of chlorine on phenols, i, 259, 317.
- azines and eurhodoles obtained from dihydroxydiketotetrahydronaphthalene, i, 356.
- Zincke, T., and O. Fuchs, conversion of the ketochlorides of resorcinol and orcinol into pentene-derivatives, i, 318.
- imido-derivatives of chlorinated diketopentene, i, 558.
- Zincke, T., and H. Günther, conversion of pentene-derivatives into indene-derivatives, i, 344.
- Zincke, T., and F. Küster, action of chlorine on catechol and orthamidophenol, i, 698.
- Zink, J. See Amthor.
- Zoja, L., uroerythrin and hæmatoporphyrin in urine, ii, 178.
- Zopf, W., crystalline acid from lichen: thamnolic acid, i, 727.
- Zumbro, E. A. See Bamberger.
- Zuntz, N., nutritive value of cellulose, ii, 22.
- Zuntz, N., and A. Magnus-Levy, digestibility and nutritive value of bread, ii, 24.
- Zuntz, N. See also Lehmann.
- Zuschlag, G. See Otto.
-

INDEX OF SUBJECTS.

ABSTRACTS. 1893. Parts I & II.

And also to Transactions, 1893 (marked TRANS.); and to such papers as appeared in the Proceedings during the Session 1892—1893 (Nos. 115 to 127; Nov., 1892, to July, 1893), but not in Transactions (marked PROC.).

A.

Abies canadensis, spruce oil from, i, 659.

Abies pectinata, occurrence of bornylic acetate in the oil of, i, 224.

— — pine needle oil from, i, 659.

Abies sibirica, occurrence of bornylic acetate in the oil of, i, 224.

Abietic acid, i, 582.

Absorption from the stomach, ii, 581.

— in the small intestine, ii, 582.

— of arsenic trisulphide in the organism, ii, 583.

— spectra of copper salts in solution, ii, 149.

Acenaphthene, oxygenated derivatives of, i, 656.

Acenaphthenone, i, 657.

Acenaphthenoneoxime, i, 657.

Acenaphthenequinone, i, 656.

Acenaphthenequinonedioxime, i, 656.

Acenaphthenequinone-hydrazone and -dihydrazone, i, 657.

Acetaldehyde, amido-, i, 187, 300.

— condensation of, with acetone, i, 8.

Acetaldehydes, trithio-, oxidation of the two, i, 684.

Acetaldoxime, modifications of, PROC., 1893, 76.

Acetaltrimethylammonium salts, i, 300.

Acetylphenylcarbamide, i, 340.

Acetamide, bromyl-, i, 305.

Acetamidoacetophenone, mono- and trichloro-, i, 532.

Acetamidoacetylidazole, i, 46.

o-Acetamidobenzaldoxime, i, 609.

o-Acetamidobenzylamine, i, 609.

o-Acetamidobenzylaniline, i, 439.

Acetamidobenzylnitrosoparatoluidine, i, 439.

Acetamidobenzylparabromaniline, i, 439.

o-Acetamidobenzylparatoluidine, i, 439.

1 : 4-Acetamidoethoxynaphthalene, i, 39.

Acetamidoindazole, i, 46.

p-Acetamidoorthonitrodiphenylamine, i, 200.

α-o-Acetamidophenylethylamine, i, 609.

Acetanhydrocitric acid, TRANS., 699.

Acetates, chlor- and brom-, decomposition of, i, 624; ii, 266.

Acetic acid, brom-, preparation of, i, 65.

— — bromination of, i, 65.

— — chlor-, action of phosphoric anhydride on, TRANS., 461.

— — — electrolysis of, i, 640.

— — — heat of combustion of, ii, 5.

— — — preparation of, i, 130.

— — — thermochemistry of, i, 624; ii, 5.

— — — depression of the freezing point of, by dissolved substances, TRANS., 1023.

— — — depression of the freezing point of sulphuric acid by, TRANS., 1027.

— — — depression of the freezing point of water by, TRANS., 1018.

— — — dibrom-, preparation of, i, 65.

— — — diiodo-, i, 307.

— — — influence of, on gaseous metabolism, ii, 21.

— — — molecular weight of, in the liquid state, TRANS., 1103.

— — — oximido-, i, 391.

— — — trichloro-, behaviour of, at a high temperature, i, 499.

— — — electrolysis of, i, 250.

— — — heat of combustion of, ii, 5.

Acetic acid, triiodo-, i, 307.
 Acetic anhydride, depression of the freezing point of acetic acid by, TRANS., 1025.
 ——— molecular weight of, in the liquid state, TRANS., 1100.
 Acetic chloride, molecular weight of, in the liquid state, TRANS., 1100.
 Acetiodamide, i, 388.
 Acetoacetic acid, action of diazobenzene on, i, 157.
 ——— derivatives of, and ethylenediamine, condensation products from, TRANS., 1310.
 3-Aceto-1-hydroxycoumarone, i, 254.
 α -Acetonaphthalide, nitration of, PROC., 1893, 8.
 Acetophenol [3' : 1] and its derivatives, i, 652.
 ——— dinitro-, i, 653.
 Acetone, action of nitric acid on, i, 303.
 ——— amido-, i, 734.
 ——— chlorination of, i, 303.
 ——— chlorisonitroso-, i, 303.
 ——— condensation of acetaldehyde with, i, 8.
 ——— condensation of, with chloral, i, 389.
 ——— condensation products of, with concentrated sulphuric acid, i, 498.
 ——— cyan-, the so-called hydrazone of, i, 315, 571.
 ——— ethylmercaptol, behaviour of, in the organism, ii, 289.
 ——— isonitroso-, physiological action of, ii, 584.
 ——— magnetic rotation of, ii, 442.
 ——— molecular weight of, in the liquid state, TRANS., 1104.
 ——— physiological action of, ii, 584.
 ——— specific gravity of aqueous solutions of, i, 7.
 ——— thiocyan-, i, 64.
 ——— volumetric estimation of, ii, 556.
 Acetonedicarboxylic acid, action of acetic anhydride on, i, 398.
 Acetonephthalimidoethylmercaptal, i, 31.
 α -Acetonicotinic acid, i, 606.
 ——— oxime, anhydride, i, 606.
 ——— phenylhydrazone anhydride, i, 606.
 Acetonitransoil, i, 161.
 Acetonitrile, dibromonitro- and diiodonitro-, i, 542.
 ——— derivatives of, i, 494.
 ——— iodo-, i, 542.
 ——— action of silver nitrite on, i, 542.
 ——— tribromo-, i, 289.
 Acetophenone, chlorisonitroso-, i, 464.

Acetophenone, condensation of, i, 512.
 ——— orthochloro-, preparation of, TRANS., 1333.
 ——— orthochloronitro-, TRANS., 1354.
 Acetophenoneorthocarboxylic acid, heptachlor-, i, 346.
 ——— hexachlor-, i, 345.
 Acetophenonecarboxylic acid hydrazone ethiodide, i, 347.
 α -Acetopyridine- β -carboxylic acid, i, 606.
 Acetorthonitrophenetoil, i, 161.
 Acetosuccinohydrazanil, i, 70.
 o-Acetotoluidines, chloro-derivatives of, i, 580.
 Acetoxime, basic bye-product formed in benzoylating, i, 464.
 ——— physiological action of, ii, 584.
 Acetylacetanamine, i, 454.
 Acetylacetone, action of ammonia and amines on, i, 454.
 ——— action of bromacetone and sodium ethoxide on, i, 623.
 ——— action of diamines on, i, 454.
 ——— action of diethylamine on, i, 454.
 ——— action of ethylamine on, i, 454.
 ——— condensation of, with carbamide, i, 129.
 ——— condensation of, with thiocarbamide, i, 129.
 ——— pentabromo-, i, 400.
 Acetylacrylic acid, perchlor-, i, 318.
 Acetylammethylcamphonitroketone, i, 109.
 p-Acetylamidohydrazobenzene, reduction of, i, 330.
 Acetylbenzylbenzamide, i, 706.
 α -Acetyl- β -benzylhydroxylamine, i, 707.
 Acetyl- β -chloroacrylic acid, dichlor-, i, 560.
 ——— trichlor-, i, 318.
 Acetylchlorhydrins, i, 4.
 Acetylchloromethylacrylic acid, dichlor-, i, 560.
 ——— trichlor-, i, 318.
 Acetylcitraconfluorescein, TRANS., 680.
 Acetyldibromothymol, i, 317.
 Acetyldichloroacrylic acid, dichlor-, i, 560.
 Acetyl-r-ecgonine, i, 446.
 Acetylene, heat of combustion of, ii, 444.
 ——— preparation of, i, 62; PROC., 1893, 15.
 Acetylenedicarboxylic acid, addition of bromine to, i, 144.
 ——— diiodide, i, 397.
 ——— formation from the dibromosuccinic acids, i, 142.
 ——— preparation of silver acetylide from, i, 121.
 Acetyl- α -eurhodole, i, 357.
 Acetylguanine, i, 309.

- Acetylhydrastinine, i, 118.
 Acetylmalic acid, i, 457.
 — active, i, 500.
 Acetylmalic anhydride, i, 458.
 — active, i, 500.
 1-Acetylmenthylamine, i, 724.
r-Acetylmenthylamine, i, 725.
o-Acetylmethamidobenzoic acid, i, 414.
 Acetylmethylamidohydrastyleneacetic acid, i, 118.
 1':3'-Acetylmethylisindazole, i, 610.
 Acetylnicotine, i, 675.
 Acetylnitrocarbazole, i, 213.
 Acetylortho-xylene, TRANS., 81.
 — brom-, TRANS., 86.
 — oxidation of, TRANS., 90.
 Acetylortho-xyleneacetoxime, TRANS., 84.
 Acetylortho-xylenehydrazone, TRANS., 79.
 Acetylortho-xylenehydroxime, TRANS., 83.
 — brom-, TRANS., 89.
 — intramolecular change of, TRANS., 85.
 Acetyl- α -oxynaphthindone, i, 338.
 Acetylparatoluyformoxime, i, 159.
 Acetylparaxylidine, i, 198.
 Acetylphenylauramine zinc thiocyanate, i, 472.
 Acetyl- β -phenylethylamine, i, 703.
 Acetylphenylhydrazine, bromination of, i, 705.
 — paramido-, i, 534.
 Acetylphenylmethylorthopiperazone, i, 705.
 Acetyl-1-phenylpyrazole, constitution of, i, 179.
 Acetylphthalazone, i, 372.
 Acetyl- α -succinylphenylhydrazine, i, 705.
 Acetyltetrahydroisoquinoline, i, 529.
 Acetyltrichlorocrotonic acid, trichlor-, i, 318.
 Acetyltrichloromethylcrotonic acid, di- and tri-chloro-, i, 260.
 Acetyltrimethylammonium salts, i, 298.
 Acetyltriphenylphenol, i, 219.
 Acetylurethane, chlor-, i, 129.
 — dichlor-, i, 129.
 — trichlor-, i, 129.
 Acetyl-xanthamide, i, 129.
 Acetylxylenol, TRANS., 110.
 Acetylxyloylformoxime, i, 160.
 β -Achroglobin, i, 60.
 γ -Achroglobin, a new respiratory globulin, i, 236.
 δ -Achroglobin from the blood of certain mollusca, i, 615.
 Achroodextrin, i, 127.
 Acid-amides, action of thionyl chloride on, i, 553.
 Acid-chlorides, action of zinc ethide on, i, 124.
 Acids, active, influence of metals on the specific rotation of, TRANS., 296.
 — affinity of, ii, 157.
 — and bases, distribution of, in a solution containing calcium, magnesium, and carbonic and sulphuric acids, TRANS., 696.
 — weak, electrical conductivity of mixtures of, ii, 356.
 — avidity of, in aqueo-alcoholic solution, ii, 157.
 — bibasic, electrolytic synthesis of, i, 394.
 — complex inorganic, ii, 378.
 — estimation of, by calcium carbonate, ii, 342.
 — fatty, action of phosphoric anhydride on, TRANS., 452.
 — brominated, action of alkali nitrites on, i, 65.
 — preparation of, i, 65.
 — estimation of insoluble, ii, 308.
 — substitution in, i, 64.
 — vapour pressures of, ii, 446.
 — feeble, relative strengths or avidities of, PROC., 1893, 144.
 — feebly dissociated, dissociation measurements of, ii, 62.
 — free, estimation of, in presence of acid phosphates, ii, 41.
 — from Baku petroleum, i, 209.
 — from beet leaves, ii, 85.
 — gas-volumetric estimation of, ii, 87.
 — heat of dissociation of, ii, 259.
 — heat of combustion of, ii, 59.
 — in beer, estimation of, ii, 53.
 — isomeric, specific gravities of, i, 11.
 — occurring in petroleum, i, 268.
 — organic, action of potassium permanganate on, i, 251.
 — behaviour of, at high temperatures, i, 512.
 — coefficients of affinity of, ii, 407.
 — gas-volumetric analysis of, ii, 307.
 — influence of boric acid on the electrical conductivity of aqueous solutions of, ii, 506.
 — substituted, electrolysis of, i, 640.
 — polybasic, action of sulphur on, in presence of water, ii, 205.
 — unsaturated fatty, addition of chlorine to, i, 142.
 — standardising, ii, 232.
 — employment of borax for, ii, 233.
 — stereoisomeric, electrolytic conductivity of, ii, 152.

- Acids, titration of, with metallic sodium, ii, 550.
 — unsaturated, formation of pyridine derivatives from, TRANS., 874.
 — intramolecular changes in, i, 189.
 — obtained by boiling the unsaturated β -acids with soda, i, 688.
 Aconite alkaloids, TRANS., 443, 491, 991, 994.
 Aconitine aurochloride, some modifications of, TRANS., 994.
 — α -aurochloride, TRANS., 995.
 — β -aurochloride, TRANS., 996.
 — γ -aurochloride, TRANS., 997.
 — composition of commercial specimens of, TRANS., 491.
 — conversion of, into isaconitine, TRANS., 991.
 Acridine, a new, i, 350.
 — chlor-, i, 650.
 Acridine-dyes, formation of, i, 470.
 Acridol, i, 650.
 Acridone, i, 649.
 Acridylpropionic acid, i, 350.
 Acrylamide, i, 695.
 Acrylic acid, preparation of, i, 548.
 Acrylic anhydride, i, 688.
 Acrylic chloride, i, 549.
 — action of, on alcohols and phenols, i, 688.
 Acrylonitrile, i, 682.
 Adelite, ii, 420.
 Adenine, constitution of, i, 736.
 Adipin ketone, i, 555.
 — from wood oil, i, 556.
 Adipinketoxime, i, 556.
 Adonite, i, 481.
 Adonitol, i, 291.
 Affinities, determination of, ii, 64.
 Affinity, explanation of, ii, 266.
 Affinity-coefficients of aromatic amidosulphonic acids, ii, 450.
 — of organic acids, ii, 407.
 — of organic bases, ii, 407.
 — of pyrroline and indole acids, i, 42.
Agave Americana, sugar from, i, 64.
 Agavose, i, 64.
 Agriculture, employment of ferrous sulphate in, ii, 142.
 Aguilarite, ii, 214.
 Air, amount of carbonic anhydride in the, ii, 67.
 — density of, ii, 515.
 — estimation of small quantities of fire-damp in, ii, 487.
 — expired, toxic action of, ii, 223.
 — of buildings, estimation of carbonic anhydride in, ii, 240.
 Alabandine from Arizona, ii, 578.
 Alban, i, 225.
 Albene, i, 225.
 Albumin, alcohol as a substitute for, ii, 328.
 — amount of, required for the human body, ii, 328.
 — behaviour of hydrochloric acid to, i, 233.
 — chromic acid as a reagent for, in urine, ii, 200.
 — deposition of, during the fattening of full grown calves, ii, 25.
 — detection of, in urine, ii, 399, 610.
 — production of, in plants, ii, 224.
 — supposed presence of, in the walls of vegetable cells, ii, 180.
 — transformation of the, of the urine in Bright's disease, ii, 30.
 Albuminuria, carbonated, ii, 221.
 Albumose, cryoscopy of, i, 680.
 — estimation of, in peptone, ii, 146.
 Albumoses and peptone, i, 233, 741.
 — diffusibility of, i, 234.
 — nutritive value of, ii, 539.
 Alcaptonuria, ii, 82.
Alchemilla vulgaris, analysis of, ii, 593.
 Alcohol, action of sodium on, at very low temperatures, ii, 113.
 — and water, distillation of mixtures of, ii, 347.
 — as a substitute for albumin, ii, 328.
 — cryoscopic behaviour of solutions of, in benzene, ii, 110.
 — ebulliscopic analysis of, ii, 347.
 — nutritive value of, ii, 24.
 — temperatures of maximum density of aqueous solutions of, ii, 61.
 — transmission of, to milk, ii, 219.
 Alcohols, action of anhydrous hydrogen fluoride on, i, 186.
 — fatty, action of zinc chloride on, i, 382.
 — condensation of, with aromatic hydrocarbons, i, 634.
 — molecular refractive power of, ii, 57.
 — formation of benzoates from, i, 186.
 — heats of combustion of, ii, 59.
 — hydrates of, i, 291.
 — in fusel oil, i, 63.
 — influence of the constitution of, on the velocity of etherification, ii, 158.
 — secondary, ethereal hydrogen sulphates from, i, 495.
 — unsaturated, action of mercury salts on, i, 450.
 Aldehyde sulphite, presence of, in wine, ii, 189.
 Aldehydecollidine, action of bromine on, i, 43.
 — oxidation of, i, 175.
 Aldehydes, condensation of β -benzoyl-phenylhydrazine with, i, 86.

- Aldehydes, condensation of, with amido-phenols and amidophenyl ethers, i, 78.
 — fatty, condensation of, with cyan-acetic acid, i, 455.
 — from terpenes, i, 360.
 — heats of combustion of, ii, 59.
 — physiological action of, ii, 584.
 Aldoximes, aromatic, action of isocyan-ates on, i, 707.
 — isomeric, action of phenylhydr-azine on, i, 87.
 — molecular refraction of, ii, 401.
 — paraffinic, isomerism of, PROC., 1893, 76.
 — physiological action of, ii, 584.
 — stereoisomeric, hydrochlorides of, i, 411.
 α - and β -Aldoximes, discrimination be-tween, i, 87.
 Aldureides of ethylic acetoacetate and ethylic oxalacetate, i, 645.
 Algæ, fixation of free nitrogen by, ii, 336.
 Alizarin, amido-, action of formalde-hyde on, i, 573.
 — benzenesulphonate, i, 478.
 — methyl ether, TRANS., 1164, 1174.
 — preparation of, from chay root, TRANS., 1162.
 Alizarin-blue-green, i, 671.
 Alizarin-green, i, 671.
 Alizarin-indigo-blue, i, 671.
 Alkachlorophyll, i, 41.
 Alkali arsenites, volumetric estimation of the alkalis in, ii, 598.
 — metals, method of obtaining per-sistent spectra of, TRANS., 139.
 — — ultra-red spectra of, ii, 313.
 — salts, electrolysis of, ii, 441.
 — molecular volumes of dis-solved, ii, 264.
 — — toxicity of certain, ii, 179.
 Alkalimetry, gas-volumetric, ii, 91.
 — use of potassium tetroxalate in, ii, 233.
 Alkalis, estimation of, in silicates, ii, 436.
 — standardisation of, ii, 232.
 Alkaloid, deliquescent, from *Lupinus albus*, i, 739.
 — from *Corydalis cava*, TRANS., 485.
 Alkaloids, detection of, ii, 606.
 — estimation of, ii, 608.
 — of aconite, TRANS., 443, 491, 991, 994.
 — of cod liver oil, ii, 290.
 — of *Gelsemium sempervirens*, i, 614.
 — of the Papaveraceæ, i, 490.
 — of the seeds of *Lupinus albus*, i, 379.
 — volumetric estimation of, ii, 146, 199, 252, 606.
 Alkylamines, compounds of, with water, TRANS., 141.
 Alkylanilines, assay of, ii, 605.
 Alkylie acetoacyanacetates, condensation of, with phenol, i, 456.
 — benzenazocyacacetates, i, 465.
 — carbamates, action of thionyl chlor-ide on, i, 696.
 — iodides, action of hydrazine hydr-ate on, i, 411.
 — tartrates, i, 73.
 Alkylorthodiamines, i, 199.
 Allenylallylene, i, 239.
Allium cepa, essential oil of, i, 104.
— sativum, essential oil of, i, 103.
 Allocinchonine, i, 738.
 Alloxan, thermochemistry of, ii, 361.
 Alloxan-derivatives, action of orthamido-ditolylamine on, i, 324.
 Alloxanylorthamidoditolylamine, i, 325.
 Alloys of tin and iron, ii, 211.
 — separation and estimation of tin, antimony, lead, and copper in, ii, 95.
 — ternary, ii, 15, 415, 522.
 Allyl and propenyl derivatives, thermo-chemistry of isomeric, ii, 153.
 Allylene, heat of combustion of, ii, 444.
 Allylic alcohol, action of mercuric chlor-ide on, i, 450.
 — — heat developed by the union of bromine with, ii, 444.
 — — molecular weight of, in the liquid state, TRANS., 1103.
 — bisulphide, i, 104.
 — bromide, heat developed by the union of bromine with, ii, 444.
 — thiocarbimide, molecular weight of, in the liquid state, TRANS., 1100.
 Allylideneorthamidobenzylic alcohol, i, 23.
 Allylindolecarboxylic acid, i, 704.
r-Allylmethylthiocarbamide, i, 725.
 Allylmesitylthiocarbamide, i, 32.
 Allylmethylethylcarbinol, i, 544.
 Allylmethylhexylcarbinol, i, 544.
 Allylmethylindole, i, 704.
 Allylmethylindolecarboxylic acid, i, 704.
 Allylparatolylhydrazine, i, 704.
 Allylphenylhydrazine, unsymmetrical, derivatives of, i, 704.
 Allylphenylhydrazone, thionyl-, i, 704.
 Allylpropenyls, stereoisomeric, i, 238.
 Allylpropyl bisulphide, i, 104.
 Allyltolylhydrazine, derivatives of, i, 704.
Alternaria tenuis, fixation of nitrogen by, ii, 430.
 Alum, absorption of radiant heat by, ii, 5.
 Alumina, action of a high temperature on, ii, 167.
 — preparation of, ii, 324.

- Aluminates, alkali, decomposition of, by carbonic anhydride, ii, 279.
 ——— decomposition of, in presence of alumina, ii, 278.
- Aluminium amalgam, action of, on ethylic iodide, i, 622.
 ——— and its alloys, assay of, ii, 48.
 ——— apparatus in the laboratory, ii, 162.
 ——— behaviour of, towards mercuric salts, ii, 376.
 ——— chloride, preparation of, ii, 11.
 ——— synthesis with, i, 505, 718.
 ——— chromium, and iron, separation of, ii, 49.
 ——— estimation of, in bone black, ii, 498.
 ——— estimation of, in ferroaluminium, ii, 96, 243, 391.
 ——— estimation of, in steel, bronze, &c., ii, 49, 243.
 ——— estimation of silicon in, ii, 48.
 ——— incomplete oxidation of, ii, 572.
 ——— iron, manganese, zinc, and calcium, separation of, ii, 600.
 ——— phosphate, natural, formation of, ii, 537.
 ——— precipitation of, in presence of lithium, ii, 95.
 ——— separation of iron from, ii, 304, 346.
 ——— spectrum of, ii, 313.
 ——— sulphide, preparation of, ii, 169.
 ——— sulphate, basic, ii, 456.
 ——— volatilisation of, in the electric arc, ii, 508.
- Aluminium-bismuth-silver alloys, ii, 416.
- Aluminium-bismuth-tin alloys, ii, 415.
- Aluminium-lead-silver alloys, ii, 416.
- Aluminium-lead-tin alloys, ii, 415.
- Alums, anhydrous, isomorphism amongst, ii, 572.
- Amalgams, influence of frictional electricity on the formation of, ii, 441.
- Amalic acid, thermochemistry of, ii, 361.
- Amaric amide, i, 590.
- Amethylcamphonitroketone, derivatives of, i, 109.
 ——— tinctorial properties of, i, 110.
- Amides, action of thionyl chloride on, i, 553.
 ——— halogen substitution products of, i, 388.
 ——— heats of combustion of, ii, 59.
- Amido-acids, heats of combustion of, ii, 59.
- Amidoazobenzene, thionyl-, i, 517.
- Amidosulphonic acids, affinity coefficients of, ii, 450.
- Amidoximes, action of benzenesulphonic chloride on, i, 332.
- Amidoxylic acids, i, 502.
- Amines, action of alkyl iodides on, i, 128.
 ——— action of metaphosphoric acid on, i, 452.
 ——— aromatic, action of phosphorus oxychloride and thiochloride on, i, 323.
 ——— bromination of, i, 705.
 ——— benzenoid, relations between constitution and physical constants in the case of, *PROC.*, 1893, 41.
 ——— conversion of, into diazoimides by the means of azoimide, i, 202.
 ——— cryoscopic behaviour of acetates of, i, 667.
 ——— heats of combustion of, ii, 59.
 ——— molecular depression of the freezing point of water produced by, *TRANS.*, 185.
- Ammonia, action of, on hypochlorites, ii, 317.
 ——— action of, on metallic sulphates, ii, 118.
 ——— action of sulphuric acid on, at very low temperatures, ii, 113.
 ——— and methylamines, analysis of mixtures of, ii, 104.
 ——— compounds of, with water, *TRANS.*, 141.
 ——— detection of, with Nessler's reagent, ii, 301.
 ——— freezing points of aqueous solutions of, *TRANS.*, 181.
 ——— in rain, ii, 548.
 ——— liquid, specific heat of, ii, 258.
 ——— occurrence of, in the stomach contents, ii, 177.
 ——— reactions of, at low temperatures, ii, 469.
- Ammonio-metallic compounds, constitution of, ii, 379.
 ——— cryoscopy, &c., of, ii, 156.
- Ammonium chloride, non-formation of, from dry ammonia and hydrogen chloride, ii, 463; *PROC.*, 1893, 129, 165.
 ——— chromates, ii, 17.
 ——— dextroethoxysuccinate, *TRANS.*, 236.
 ——— dextromethoxysuccinates, *TRANS.*, 225.
 ——— glycerate, active and inactive, *TRANS.*, 304.
 ——— hydrogen dextroethoxysuccinate, *TRANS.*, 231.
 ——— levomethoxysuccinate, *TRANS.*, 338.
 ——— hydrosulphide, *PROC.*, 1893, 178.
 ——— lead chlorides, ii, 523.
 ——— haloïds, ii, 523.
 ——— magnesium urate, ii, 99.

- Ammonium molybdo-sulphite, ii, 530.
 — nitrite, influence of electrolytic dissociation on the decomposition of, in aqueous solution, ii, 155.
 — permanganate, ii, 325.
 — persulphate as an oxidising agent, i, 640.
 — — preparation of, ii, 516.
 — plumbichloride, ii, 415, 523.
 — seleniobromide, ii, 318.
 — sulphate and sodium nitrate, relative value of, as manures for barley and oats, ii, 523.
 — — detection and estimation of thiocyanates in, ii, 556.
 — sulphide, oxidation of solutions of, PROC., 1893, 178.
 — sulphides and polysulphides, PROC., 1893, 178.
 — tetrachromate, ii, 528.
 — thiocyanate, estimation of, in nitrogenous manures, ii, 347.
 — — thermochemistry of, ii, 359.
 — trithionate, i, 703.
 Amygdalin, behaviour of, in the organism, ii, 329.
 Amylamide, bromyl-, i, 305.
 Amylamine, ϵ -brom-, i, 10.
 — freezing point of aqueous solutions of, TRANS., 179.
 — tertiary, action of tertiary butyl iodide on, i, 128.
 — thionyl-, i, 504.
 Amylanisoil, i, 563.
 Amylase, ii, 587.
 Amylbenzene, i, 543.
 Amylene, action of nitrosyl chloride on, TRANS., 482.
 — behaviour of, with zinc chloride, i, 382.
 — commercial, composition of, i, 381.
 — critical temperature of, ii, 446.
 — formation of amylic salts by the action of acids on, i, 449.
 — hydrate, influence of, on metabolism, ii, 543.
 — magnetic rotation of, ii, 442.
 — "mixed," alcohol and other products from, i, 141.
 Amyleneglycol, new, i, 541.
 Amylenes, hydration of, i, 61.
 Amylic alcohol, active, preparation of, from fusel oil, TRANS., 1130.
 — — specific volume and thermal expansion of, TRANS., 282.
 — — fourth primary, i, 542.
 — — inactive, specific volume and thermal expansion of, TRANS., 281.
 — — magnetic rotation of, ii, 442.
 — — molecular weight in the liquid state, TRANS., 1102.
 — — normal, i, 542.
 Amylic ether, magnetic rotation of, ii, 442.
 — pyruvate, i, 627.
 — trichloracetate, i, 450.
 Amyloid, i, 447.
 — vegetable, i, 127.
 Amyloid-substance, i, 288.
 Amylphenol [1:4], i, 215.
 — tertiary, i, 563.
 Amylpseudonitrol, i, 243.
 Amylthionamic acid, i, 505.
 Anæsthesia, gases of blood during, ii, 540.
 "Analgen," isomerides and congeners of, i, 606.
 Analysis, electrolytic, electromotive force in, ii, 506.
 — electrometric, ii, 387.
 — quantitative, by electrolysis, ii, 391, 496.
 — volumetric, use of potassium hydrogen tartrate in, ii, 144.
 Andirine, i, 182.
Andropogon schænanthus, essence of, i, 664.
 Anemonin and its occurrence, i, 727.
 Anethoil, thermochemistry of, ii, 154.
 Angelic acid, brom-additive products of, i, 135, 155, 188.
 — — constitution of, i, 141.
 — — dibromide, i, 136.
 — — index to the literature of, i, 10.
 — — preparation of, i, 135.
 Anglesite associated with boléite, ii, 326.
 Anhydrides, action of alkali alkyl oxides on, i, 362.
 — heats of combustion of, ii, 59.
 Anhydrite as a sublimation product, ii, 18.
 Anhydroecgonine, constitution of, i, 377.
 — ethyl ether, derivatives of, i, 378.
 Anhydromuscarine, i, 297.
 Anilides which exist in two modifications, i, 511.
 β -Anilidoacrylic acid, i, 565.
 Anilidobenzeneindone, i, 266.
 Anilidobenzeneinduline, i, 266.
 γ -Anilidobutyronitrile, i, 9.
 Anilidohydroxydiketotetrahydronaphthalene, i, 221.
 α -Anilido- α -hydroxynaphthaphenazine, i, 357.
 B₂-4-Anilidoinduline, i, 335.
 Nt₃-2'-Anilido- $\alpha\beta$ -isorosinduline, i, 336.
 α -Anilido- α -ketoidene, pentachlor-, i, 345.
 Anilidomethyleneglutaconic acid, i, 402.
 Anilidonaphthaquinonedianil, i, 338.
 $\alpha\beta$ -Anilidonaphthindone, i, 338.
 $\alpha\beta$ -Nt₃-4-Anilidonaphthindone, i, 337.
 $\alpha\beta$ -Nt₃-4-Anilidonaphthinduline, i, 337.

- m*-Anilidoparanitrophenetol, i, 328.
m-Anilidoparanitrophenol, i, 328.
m-Anilidoparaphenetidine, and its derivatives, i, 328.
 Nt₂-2'-Anilidophenyl- $\alpha\beta$ -isorosinduline, i, 336.
 $\alpha\beta$ -Anilidophenyl-naphthylinduline, symmetrical, i, 338.
 Anilidophenylquinonediimide, i, 266.
 Anilidoquinonephenylimide, i, 267.
 Anilidosalicylic acid, i, 211.
 ——— diamido-, i, 211.
 ——— dinitro-, i, 211.
 ——— nitramido-, i, 211.
 Anilidosuccinic acid, dinitroso-, i, 565.
 Aniline, action of ammonium hydrogen sulphate on, i, 411.
 ——— action of hydrogen peroxide on, i, 197.
 ——— and its homologues, relations between constitution and physical constants with, *PROC.*, 1893, 41.
 ——— bromosalicylate, i, 211.
 ——— chlorobrom- [2:5], i, 321.
 ——— direct conversion of, into nitrobenzene, i, 323.
 ——— gallate, i, 167.
 ——— hydrogen malate, i, 264.
 ——— methylaniline and dimethylaniline, estimation of, i, 23.
 ——— molecular weight of, in the liquid state, *TRANS.*, 1101.
 ——— oil, analysis of, ii, 605.
 ——— thionyl-, i, 515.
 ——— chloro-, i, 515.
 Anilineazoquinol, i, 571.
 ——— paranitro-, i, 571.
 Anilines, monobromo-, isomeric, i, 21.
 ——— thermochemistry of, i, 22.
 ——— thionyl-, chloro-, bromo-, iodo-, and nitro-derivatives of, i, 515.
 Anilpapaverinic anilide, i, 181.
 Animals, peptonised, gaseous tension in the blood and serum of, ii, 131.
 Animal-tissues, complete process of reduction occurring in, ii, 544.
 Anisaldehydephenolparathionamic acid, i, 517.
 α -*p*-Anisaldoxime, action of phenylhydrazine on, i, 87.
 α -Anisaldoxime ethyl ether, action of phenylhydrazine on, i, 88.
 Anisaldoximes, action of hydrochloric acid and ammonia on, i, 411.
 Anisic acid, thioanilide of, i, 154.
 Anisidine, orthothionyl-, i, 517.
 Anisoil, action of cinnamic chloride on, i, 164.
 ——— action of phenylthiocarbimide on, i, 154.
 ——— preparation of, i, 639.
 ——— thermochemistry of, ii, 154.
 Anisoles, i, 274.
 Anisyl phenyl ketone, hydrazones of, i, 208.
 Anisylphenyl ketochloride, action of amidodimethylaniline on, i, 409.
 Anniversary meeting, *TRANS.*, 739.
 Anthracene series, Friedel-Crafts reaction in the, i, 358.
 Anthragalloil dimethyl ethers, *TRANS.*, 1163, 1168, 1172.
 ——— methyl ether, *TRANS.*, 1170.
 Anthrapurpurin benzenesulphonate, i, 478.
 Anthraquinolinequinone, hydroxy-derivatives of, i, 670.
 Antimony, action of hydrochloric acid on, ii, 126.
 ——— ammonium fluoride, ii, 373.
 ——— and copper, simultaneous precipitation of, by the galvanic current, ii, 72.
 ——— chlorosulphides, ii, 533.
 ——— copper, and tin, analysis of an alloy of, ii, 242.
 ——— lead, and tin, separation of, ii, 95.
 ——— detection of, ii, 192.
 ——— electrolytic estimation of, ii, 95.
 ——— electrolytic separation of copper from, ii, 495.
 ——— estimation of, ii, 90.
 ——— estimation of, in alloys, ii, 95.
 ——— iodosulphides, ii, 533.
 ——— separation of arsenic from, ii, 186, 600.
 ——— trioxide, action of potash and soda on, ii, 171.
 ——— ——— estimation of, ii, 90.
 ——— trisulphide, black, ii, 473.
 ——— volumetric estimation of, ii, 492, 554.
 Antimony-bismuth-zinc alloys, ii, 522.
 Antimony-lead-zinc alloys, ii, 522.
 Antimonyl potassium tartrate, stability of standard solutions of, ii, 600.
 Antiseptics, influence of, on fermentation, ii, 32.
 Apiole, thermochemistry of, ii, 154.
 Apotropine, belladonnine, and atropine, the relation between, i, 491.
 Apocinchene, oxidation products of, i, 376.
 Apocinchonine, i, 678.
 ——— hydrochloro-, i, 678.
 Apocotinine, i, 444.
 Apoisochinchonine, i, 677.
 ——— hydrochloro-, i, 677.
 Aposafranine, i, 613.
 Apparatus of aluminium for laboratory use, ii, 162.
 Apples, chemical composition of, ii, 37.

- Apricots, Californian, analyses of, ii, 140, 591.
 Arabin, i, 295.
 — mononitrate, i, 294.
 — dinitrate, i, 294.
d-Arabinose, i, 293.
i-Arabinose, i, 294.
l-Arabinoseoxime, i, 294.
 Aragonite, heat of formation of, ii, 259.
 Aromatic alkyl ketones, i, 162.
 — iodochlorides, i, 149.
 — silicates, action of phosphorus oxychloride on, i, 74.
 — sulphonic acids, constitution of the iodides of, i, 269.
 Arsenates and arsenites, action of sulphur and water on, ii, 205.
 — crystalline, ii, 273.
 — precipitation of, by ammonium molybdate, ii, 45.
 Arsenic acid, Fleitmann's test with, TRANS., 884.
 Arsenic and antimony, separation of, ii, 186, 600.
 — cesium haloids, ii, 572.
 — chloride, melting point of, ii, 357.
 — chlorosulphides, ii, 533.
 — detection of, ii, 192.
 — estimation of, ii, 299.
 — improvements in Reinsch's test for, TRANS., 886.
 — iodide, solubility of, in methylenic iodide, ii, 378.
 — iodosulphides, ii, 533.
 — precipitation of, as pentasulphide, ii, 186.
 — quantitative conversion of, into hydrogen arsenide, ii, 186.
 — rubidium haloids, ii, 572.
 — separation of, from antimony, bismuth, cadmium, and lead, ii, 186.
 — sublimation of, ii, 570.
 — trisulphide, absorption and physiological action of, ii, 583.
 — volumetric estimation of, ii, 554.
 Arsenical pyrites, ii, 418.
 Arsenious anhydride, action of, on the animal organism, ii, 136.
 — compounds of, with cesium, potassium, and rubidium haloids, ii, 572.
 — compounds of, with sulphuric anhydride, ii, 66, 459.
 — estimation of, ii, 90.
 — transformations of, in the organism, ii, 583.
 Arsenites, alkali, volumetric estimation of the alkali in, ii, 598.
Artemisia gallica, occurrence of betaïne and choline in, ii, 485.
 Artichokes, Jerusalem, alcoholic fermentation of, with pure yeast, ii, 482.
 — — — carbohydrates of, i, 617.
 Asarone, thermochemistry of, ii, 154.
 Ash of plants, estimation of fluorine in, ii, 234.
 Asparagine, nutritive value of, ii, 27, 177.
 — physiological action of, ii, 27.
 Asparagus root, reserve proteid of, ii, 431.
Aspergillus niger, fixation of nitrogen by, ii, 429.
Aspidium filix mas, ethereal oil from the root of, i, 625.
 Assay of gold bullion, limits of accuracy attained in, TRANS., 700.
 Astochite, ii, 421.
 Asymmetry, product of, ii, 561.
 Aticonic acids, i, 691.
 Atmospheres, speed of vaporisation of compounds in different, ii, 564.
 Atomic refraction of phosphorus, ii, 353.
 — — — of the elements with respect to sodium light, ii, 253.
 Atomic weight, determination of, by the method of limit, ii, 316.
 — — — determinations, collective discussions of, TRANS., 37.
 — — — from the time of Berzelius to that of Stas, TRANS., 22.
 — — — from 1860 to 1881, TRANS., 37.
 — — — list of papers by Stas on, TRANS., 36.
 — — — methods desirable to be pursued in, TRANS., 46.
 — — — since 1882, list of papers on, TRANS., 38.
 — — — general method for the calculation of, from the data of a chemical analysis, ii, 317.
 — — — of barium, ii, 463.
 — — — of boron, ii, 207; TRANS., 209.
 — — — of cadmium, ii, 168.
 — — — of carbon, ii, 165.
 — — — of cobalt, ii, 469, 574.
 — — — of contained metals, and the magnitude of the angles of crystals of isomorphous series, connection between, TRANS., 337.
 — — — of copper, ii, 12.
 — — — of lead, Stas's determinations of, ii, 277.
 — — — of nickel, ii, 212, 469, 574.
 — — — of oxygen, ii, 163.
 — — — of palladium, ii, 73, 284.
 — — — of thallium, ii, 322.
 — weights, new system of, ii, 267.
 — — — of the elements, early history of investigation as to, TRANS., 16.

Atomic weights, Stas' determinations of, ii, 451; TRANS., 24.
 Atoms, specific heat and mechanical constitution of, ii, 59.
 — the measurement of the relative masses of the, of the chemical elements, TRANS., 1.
 Atropine, apoa tropine, and belladonnine, relation between, i, 491.
 — effect of, on the action of the kidney, ii, 542.
 — physiological action of, ii, 222.
 Augite in a Minnesota gabbro, ii, 78.
 Augites, ii, 130.
 Auramines, i, 472.
 Aurochlorocaffeine, TRANS., 201.
 Aurosoauricchloride and bromide, ii, 126.
 Avidities of some compounds of weak acid character, PROC., 1893, 144.
 Avidity of acids in aqueo-alcoholic solution, ii, 157.
 Azelaic acid, ketone from, i, 558.
 — — synthesis of, i, 695.
 Azine dyes, synthesis of, i, 15.
 Azines, ammonium derivatives of, i, 282.
 — from dihydroxydiketotetrahydro-naphthalene, i, 356.
 — of the lapachol group, TRANS., 1376.
 Azallyltolyl, i, 704.
 Azobenzene, origin of colour in, PROC., 1892, 194.
 — periodo-, reduction of, i, 330.
o-Azobenzenedicarboxylic acid, i, 210.
 Azobenzeneinduline, amido-, i, 335.
 4-Azobenzenepyrazolone, i, 428.
 Azobenzenepyrazolonecarboxylic acid, i, 367.
 Azobenzoic acid, action of phosphoric chloride on, i, 165.
 Azobenzyl alcohols, ortho- and para-, i, 201.
 Azocarmine, i, 339.
 Azo-compounds, heats of combustion of, ii, 59.
 — — meta-, PROC., 1893, 126.
 — — mixed, i, 84.
 — — nitramido- and nitrohydroxy-, i, 570.
 — — of the ortho-series, TRANS., 923.
 — — — ortho-, constitution of, TRANS., 936.
 — — — reduction products of, i, 327.
o-Azodibenzylaniline, i, 201.
o-Azodibenzylparatoluidine-, i, 201.
 Azo-group, intramolecular formation of, i, 201.
 Azoimide, formation of, from aromatic azoimides, i, 90.
 — new synthesis of, i, 463.
 — preparation of, ii, 372.

Azosalphonic acids, nitramido- and nitrohydroxy-, preparation of, i, 570.
p-Azotoluene, preparation of, TRANS., 1398.
 Azoxybenzoic acids, i, 164.
 — — action of phosphoric chloride on, i, 165.

B.

Bacillus pluvialis, ii, 83.
 — *radicalicola*, fixation of nitrogen by, ii, 588.
 Bacteria, fixation of nitrogen by, ii, 429.
 — leguminous, power of propagation of, in a soil, ii, 32.
 — of the stomach, ii, 223.
 Bacterium in urine, production of hydrogen sulphide and methyl mercaptan by, ii, 335.
 Bacteroids, ii, 590.
 — the assimilation of free nitrogen by Leguminosæ connected with the production of, ii, 588.
 Balance sheet of the Chemical Society, from March 18th, 1892, to March 16th, 1893, TRANS., 748.
 — — of the Research Fund, from March 18th, 1892, to March 16th, 1893, TRANS., 749.
 Barbituric acid, thermochemistry of, ii, 360.
 Barium and strontium bromides, separation of, by means of amyl alcohol, ii, 241.
 — arsenates, ii, 273.
 — atomic weight of, ii, 463.
 — calcium and strontium, separation of, ii, 436.
 — chloride, preparation of, i, 62.
 — carbonate, solubility of, ii, 520.
 — dextroethoxysuccinate, TRANS., 235.
 — dextromethoxysuccinate, TRANS., 226.
 — elimination of, from strontium salts, ii, 209.
 — estimation of, in presence of calcium and strontium, ii, 47.
 — flame spectrum of, ii, 402.
 — fluoride, ii, 414.
 — glycerate, active and inactive, TRANS., 298.
 — oxide, action of a high temperature on, ii, 167.
 — permanganate, ii, 324.
 — peroxide, estimation of, ii, 86.
 — — dissociation of, ii, 71.
 — sulphate, influence of nitric acid and aqua regia on the precipitation of, ii, 552.
 — — retention of iron salts by, ii, 73.

- Barium sulphate, solubility of, ii, 520.
 ——— treatment of, in analysis, ii, 552.
 ——— sulphite, ii, 456.
 ——— zincoxide, ii, 118.
 Barium-group, quantitative separation of, ii, 92.
 Barley, assimilation of nitrogen by, ii, 33.
 ——— occurrence of betaïne and choline in the sprouts of, i, 684.
 ——— relative value of ammonium sulphate and sodium nitrate as manures for, ii, 593.
 Bases and acids, distribution of, in a solution containing calcium, magnesium, and carbonic and sulphuric acids, TRANS., 696.
 ——— weak, dielectrical conductivity of mixtures of, ii, 356.
 ——— aromatic, spectrophotometric investigation of, i, 464.
 ——— spectrophotometric investigation of the salts of, i, 333.
 ——— from oil of polei, i, 115.
 ——— organic, action of metaphosphoric acid on, i, 452.
 ——— in the juice of flesh, i, 55.
 ——— coefficients of affinity of, ii, 407.
 Basic slag, estimation of phosphoric acid in, ii, 88.
 Batteries, secondary, chemistry of, ii, 3, 4.
 Battery, cadmium and ammonium chloride, ii, 402.
 ——— Leclanché, ii, 355, 402.
 ——— Meidinger, ii, 355.
 ——— secondary, chemistry of, ii, 150.
 Beer, detection of "saccharin" in, ii, 504.
 ——— estimation of acids in, ii, 53.
 Beeswax, analysis of, ii, 351, 397.
 ——— analysis of, by Hübl's method, ii, 198.
 Beet, effect of phosphate manuring on the amount of sugar and the value of, ii, 228.
 ——— acid from leaves of, ii, 85.
 Behenic acid, i, 548.
 Behenic acid, i, 551.
 ——— action of sulphuric acid on, i, 393.
 ——— oxidation products of, i, 305.
 Belladonnine, atropine, and apatropine, the relation between, i, 491.
 Benzal chloride, orthochloro-, condensation of, i, 351.
 Benzalacetonephthol, i, 652.
 Benzalacetosodiumphthol, i, 652.
 Benzalimidacetal, i, 360.
 4-Benzalazipyrazolone-3-carbonylbenzalhydrazine, i, 730.
 Benzaldehyde, action of amides on, i, 712.
 ——— action of, on ethylic oxalacetate, i, 714.
 ——— carbamide and ethylic acetoacetate, interaction of, i, 649.
 ——— condensation of, with acetone and carbamide, i, 648.
 ——— condensation of, with β -benzoylphenylhydrazine, i, 86.
 ——— condensation of, with deoxybenzoïn, i, 353.
 ——— condensation of, with glycocine, i, 166.
 ——— condensation of, with hippuric acid, i, 167.
 ——— hydrazone of, oxidation of, i, 98.
 ——— melting point of, ii, 357.
 ——— metanitro-, conversion of, into acetamidobenzoic acid in the animal organism, ii, 544.
 ——— molecular weight of, in the liquid state, TRANS., 1101.
 ——— orthochloro-, preparation and nitration of, i, 160.
 ——— orthochloronitro-, hydrazone of, TRANS., 1353.
 ——— phenylpropylthionamate, i, 703.
 Benzaldehydeamylthionamic acid, i, 505.
 Benzaldehydedicarboxylic acid, i, 593.
 Benzaldehydeisobutylthionamic acid, i, 505.
 Benzaldehydemetachlorophenylhydrazone, TRANS., 871.
 Benzaldehydeparachlorophenylhydrazone, TRANS., 873.
 Benzaldehydephenylhydrazone, tetrazone from, i, 461.
 Benzaldehydephenolparathionamic acid, i, 517.
 Benzaldehydepropylthionamic acid, i, 505.
 Benzaldoxime, orthochloronitro-, action of alkalis on, TRANS., 1348.
 ——— preparation of, TRANS., 1347.
 ——— methyl ether, orthonitro-, i, 710.
 α -Benzaldoxime benzyl ether, action of phenylhydrazine on, i, 87.
 ——— formation of benzonitrile from, i, 89.
 ——— metanitro-, action of phenylhydrazine on, i, 87.
 ——— methyl ether, action of phenylhydrazine on, i, 88.
 β -Benzaldoxime, action of bromine on, i, 332.
 ——— ethyl ether, action of phenylhydrazine on, i, 88.

- Benzaldoximes, orthonitro-, isomeric, i, 709.
 4-Benzalpyrazolone, i, 428.
 Benzalpyrazolonecarbonylbenzaldehyde, i, 367.
 Benzalpyrazolonecarboxylic acid, i, 367.
 Benzaltetrazolyhydrazine, i, 441.
 Benzamarone, i, 589.
 — distillation of, i, 353, 589.
 — metanitro-, i, 589.
 Benzenarones, stereoisomeric, i, 352.
 Benzamide, metamido-, action of thionyl chloride on, i, 554.
 — orthamido-, derivatives of, i, 574.
 Benzamidoacetophenone, i, 531.
 Benzene, action of chloral on, i, 718.
 — action of phenylthiocarbimide on, i, 153.
 — bromo-, melting point of, ii, 357.
 — chloro-, critical temperature of, ii, 446.
 — — melting point of, ii, 357.
 — — molecular weight of, in the liquid state, TRANS., 1100.
 — condensation of, with ethyl, propyl, isobutyl, and hexyl alcohols, i, 634.
 — condensation of, with normal α -hexylene, i, 635.
 — constitution of, i, 603.
 — critical constants of, ii, 446.
 — depression of the freezing point of, by dissolved substances, TRANS., 1019.
 — depression of the freezing point of naphthalene by, TRANS., 1027.
 — di- and tri-iodochlorides, i, 149.
 — heat of vaporisation of, ii, 446.
 — hexiodo-, i, 14.
 — hydro-derivatives of, i, 255.
 — hydrogenation of, i, 150, 460.
 — iododichloride, chloro- and bromo-, i, 696.
 — — metanitro-, i, 506.
 — iodo-, m. p. of, ii, 357.
 — iodoso-, i, 149, 505, 507, 696.
 — — bromo-, i, 696.
 — — chloro-, i, 697.
 — — derivatives of, i, 149, 696.
 — — metanitro-, i, 506, 561.
 — — orthochloro-, i, 506.
 — — orthonitro-, i, 561.
 — — parabromo-, i, 257.
 — — paranitro-, i, 257, 561.
 — — reaction of, i, 256.
 — iodoxy-, i, 150, 506, 696.
 — — bromo-, i, 696.
 — — chloro-, i, 697.
 — — metanitro-, i, 506.
 — — orthochloro-, i, 506.
 — — orthonitro-, i, 561.
 — — parabromo-, i, 257.
 — — paranitro-, i, 561.
 Benzene, iodoxy-, preparation of, i, 256.
 — — magnetic rotation of, ii, 442.
 — — molecular weight of, in the liquid state, TRANS., 1100.
 — — nitro-, action of aluminium chloride on, i, 161.
 — — detection of, ii, 306.
 — — direct conversion of aniline into, i, 323.
 — — electrolytic reduction of, i, 323, 406, 566.
 — — molecular weight of, in the liquid state, TRANS., 1101.
 — — nitroso-, i, 326.
 — — orthodinitro-, preparation of, i, 256.
 — — thionylamidoazo-, i, 517.
 Benzenaezoacetylacetone, acetyl and benzoyl derivatives of, i, 84.
 Benzenaezocatechol, i, 410.
 — paranitro-, i, 410.
 Benzenaezo- β -ethylnaphthylamine, i, 284.
 Benzenaezometacresetol, reduction of, i, 330.
 Benzenaezo- α -naphthalene, i, 275.
 Benzenaezo- β -naphthol, reduction of the acetyl derivative of, TRANS., 930.
 — — parachloro-, reduction of the acetyl derivative of, TRANS., 933.
 Benzenaezoorthocresetol, reduction of, i, 330.
 Benzenaezoorthohydroxymetatoluic acid, i, 341.
 Benzenaezophenetol, reduction of, i, 327.
 Benzene-derivatives, action of nascent bromine on, i, 560.
 Benzenediazoic acid, i, 326, 327.
 Benzene- α -hydrazonaphthalene, i, 276.
 Benzeneindulines, i, 333.
 Benzene-series, cryoscopic studies in the, i, 270.
 — — metallic derivatives of, i, 508.
 Benzenesulphonamide, action of form-aldehyde on, i, 714.
 Benzenesulphonamides, i, 168.
 Benzenesulphonates, aromatic, i, 478.
 Benzenesulphoneamidoazobenzene, i, 168.
 Benzenesulphonebenzidine, i, 168.
 Benzenesulphonic acid, cryoscopic behaviour of, i, 270.
 — — nitroso-, nature of, i, 168.
 — — acids, amido- and alkylamido-affinity coefficients of, ii, 450.
 Benzenoid hydrocarbons, molecular refractive power of, ii, 57.
 Benzenylbromoximeacetic acid, i, 502.
 Benzenylchloroximeacetic acid, i, 501.
 Benzenylchloroximeglycollic acid, i, 501.

- Benzenylethyltolylenediamine, i, 286.
 Benzenylfluoroacetic acid, i, 502.
 Benzenylimidonitrile, i, 711.
 Benzenylnitritoximeacetic acid, i, 502.
 Benzethylenamide, orthamido-, i, 574.
 Benzhydrazine, orthamido-, i, 574.
 Benzhydroxametic acid, i, 502.
 Benzhydroxamic acid, stereoisomerism of, i, 510, 572, 710.
 Benzhydrylamine salts, i, 703.
 — thionyl-, i, 703.
 Benzidine, preparation of, i, 469, 470.
om-Benzidinedicarboxylic acid, i, 210.
 Benzilam, TRANS., 474.
 Benzilamidotertiarybutylphenazine, i, 637.
 Benzile, action of diorthamidodiphenyl on, i, 96.
 — chloro-, condensation of, with phenol and with mono- and di-methyl-aniline, i, 354.
 — — hydrazones of, i, 208.
 — combination of orthodiamidodiphenyl with, i, 96, 588.
 — condensation of with diamidoditolyl, i, 588.
 — reduction of, with hydriodic acid, TRANS., 770.
a-Benziledioxime, action of phenylhydrazine on, i, 97.
 Benziledioximes, i, 474.
 Benzilehydrazone, reduction of, i, 354.
 Benzenitrotertiarybutylphenazine, i, 637.
γ-Benzileoxime, action of phenylhydrazine on, i, 97.
 Benzileoximehydrazone, acetyl derivative of, i, 354.
 Benzileoximes, i, 97, 354, 474.
 — salts of, i, 354.
a-Benzilephenylhydrazine and its derivatives, i, 97.
 — oxidation of, i, 98.
 Benzimadazole, nitro-, i, 436.
 Benzimadazole-2-carboxylic acid, i, 436.
 Benzimadazole-chloral, i, 438.
 Benzimadazole-2 : 2'-dicarboxylic acid, i, 436.
 Benzimadazole-ring, opening of the, i, 437.
 Benzimadazoles, addition of chloral to, i, 438.
 — behaviour of the 2'-methyl group in, i, 435.
 — constitution and formation of, i, 433.
 Benzimidazole ethyl ether, action of hydrazine, on, i, 711.
 Benzoic acid, action of phenylic isocyanate on, i, 362.
 — — iodoso-, i, 507, 577, 713.
 — — iodoxy-, i, 577, 713.
 Benzoic acid, orthochloro- and orthobromo-, preparation of, i, 641.
 — — orthiodo-, i, 577.
 — — paraiodosometanitro-, i, 578.
 — — paraiodoxymetanitro-, i, 578.
 Benzoic acids, amido-, action of light on, i, 641.
 — — — distinction between, i, 641.
 — — — isomeric, solubility of, in various solvents, i, 413, 465.
 — — — nitro-, action of light on, i, 642.
 Benzoic anhydride, iodoso-, i, 578.
 — — preparation of, i, 92.
 Benzoic chloride, action of aluminium chloride on, i, 578.
 — — action of hydrazine hydrate on, i, 411.
 — — action of, on ammonia, ii, 145.
o-Benzoiesulphinide, detection of, ii, 606.
 — action of phosphorus pentachloride on, i, 715, 716.
 Benzoin, condensation of acetone with, i, 219.
 — gum-, i, 480, 481, 666.
 Benzonitrile, formation of, from *a*-benzaldehyde, i, 89.
 — molecular weight of, in the liquid state, TRANS., 1101.
 — orthobromo-, i, 95.
 — orthochloro-, i, 716.
 Benzoparaphenanthroline, i, 604.
 Benzophenone, ortho- and para-chloro-, hydrazones of, i, 208.
 — orthiodo-, i, 577.
 — oxime, orthobromo-, i, 95.
 Benzophenones, symmetrical, oximes of, i, 97.
 Benzo-5-phenylpyridazolone, i, 368.
 Benzophlobaphen, i, 481.
 Benzoquinone, action of hydrogen chloride on, i, 322.
 — 'chlorine and bromine additive products of, i, 320.
 Benzoresinol, and its derivatives, i, 480, 666.
 Benzoresinyl benzoate, i, 666.
 Benzotoluidide, nitroso-, i, 154.
 Benzotrichloride, orthochloro-, condensation of, i, 351.
 Benzoyl, detection of, in organic compounds, ii, 395.
 — peroxide, molecular weight of, i, 579.
 Benzoylacetic acid, action of diazobenzene on, i, 157.
 — anilide, i, 369.
 Benzoylacetone, benzoyl-derivatives of, i, 577.
 — condensation of, with carbamide, i, 129.
β-Benzoylacrylic acid, i, 302.

- Benzoylamidoacetal, i, 300.
 Benzoylamidocinnamic acid, i, 582.
 ——— sodium salt of, i, 580.
 ——— lactimide, i, 580.
o-w-Benzoylamidoethylbenzoic acid,
 i, 529.
α-Benzoylamidophenylpropionic acid,
 i, 581.
 Benzoyl-*α*-anisaldoxime, i, 88.
 ——— action of phenylhydrazine on, i, 88.
 Benzoylbenzacetoneitrile, i, 314.
 Benzoyl-*α*-benzaldoxime, i, 88.
 ——— action of phenylhydrazine on, i, 88.
 3'-Benzoylbenzimidazole, i, 437.
o-Benzoylbenzoic acid, action of hydro-
 xylamine on, i, 466, 589.
 ——— oxime, i, 467.
 Benzoylbenzylbenzamide, i, 706.
α-Benzoyl-*β*-benzylhydroxylamine,
 i, 706.
β-Benzoyl-*α*-bis-diphenylformamidyl-
 phenylhydrazine, i, 463.
 Benzoylbromocarbazole, i, 349.
 Benzoylcatechol, i, 410.
 Benzoylcinchonine, i, 678.
 Benzoyldiacetonitrile, i, 314.
 Benzoyldiazobenzene, i, 200.
 Benzoyldibromocarbazole, i, 349.
 Benzoyldibromothymol, i, 317.
 Benzoyldihydromethylketole, i, 522.
 Benzoyldiphenyl and aluminium chlor-
 ide, compound of, i, 579.
 Benzoyl-*nor-r*-ecgonine, i, 537.
 Benzoyl-*l*-ecgoninenitrile, i, 445.
 Benzoyl-*r*-ecgoninenitrile, i, 445.
 Benzoylformamide, orthobromo-, i, 95.
 Benzoylformanilide, i, 474.
 Benzoylformic acid, orthobromo-, i, 95.
 Benzoylformoxime, action of phenyl-
 hydrazine on, i, 170.
 ——— parabromo-, i, 160.
 Benzoylguanine, i, 309.
 Benzoylhydrastinine, i, 117.
i-Benzoylhydroceton, i, 718.
 Benzoylhydroisocarbostyryl, i, 529.
 Benzoylhydroxyhydrastinine hydrate,
 i, 118.
 Benzoylhydroxylamineacetic acid, i, 502.
 Benzoyl-*α*-metanitrobenzaldoxime, i, 88.
 ——— action of phenylhydrazine on,
 i, 88.
 Benzoylnicotine, i, 736.
 Benzoylnitrobromocarbazole, i, 349.
 Benzoylorthamidoacetophenone, i, 49.
 Benzoyl-*αβ*-oxynaphthindone, i, 338.
 Benzoylphenylbutylene, i, 463.
 Benzoyl-*β*-phenylethylamine, i, 703.
β-Benzoylphenylhydrazine, condensa-
 tion of, with aldehydes, i, 86.
 Benzoylpseudotropeine, derivatives of,
 i, 58.
 Benzoylquinol, i, 571.
 Benzoyltetrahydroisoquinoline, i, 529.
 Benzoyltriphenylbutyronitrile, i, 353.
 Benzylaldoxime methyl ether, ortho-
 nitro-, i, 710.
 ——— orthonitro-, i, 710.
 Benzylacetanilide, orthamido-, i, 438.
 Benzylacetoparabromaniline, orthaceto-,
 i, 439.
 Benzylacetoparatoluidide, orthamido-,
 i, 439.
 Benzylamidacetal, i, 300.
 Benzylamine, action of thionyl chloride
 on, i, 515, 703.
 ——— and phenacetyl bromide, interaction
 of, TRANS., 1355.
 ——— preparation of, TRANS., 1311.
 ——— sulphate, orthonitro-, i, 415.
 Benzylaminophenylsulphone, i, 204.
 Benzylaniline dihydrochloride, ortho-
 amido-, i, 439.
 Benzylanilinephenylsulphone, i, 204.
 Benzylbenzaldoxime, i, 706.
 ——— action of phenylcarbimide on,
 i, 203.
o-Benzylbenzamide, i, 16.
o-Benzylbenzylamine, i, 16.
 Benzylchloramine, i, 296.
 Benzyldeoxybenzoïn, iodo-, i, 351.
 Benzyldechloramine, i, 296.
 Benzyl dihydroxypyridine, TRANS., 259.
 Benzyl dimethylpyrimidine, i, 735.
 4-Benzyl-2 : 6-diphenylpiazine dihydr-
 ide, TRANS., 1366.
 ——— hydrochloride, TRANS., 1373.
 5-Benzyl-2 : 6-diphenylpiazine, TRANS.,
 1372.
 Benzylethylamine, orthonitro-, i, 51.
 Benzylethylformamide, orthonitro-,
 i, 51.
 Benzylfumarimide, i, 264.
 Benzylhydroxylamine benzylthiohydr-
 oxylamate, i, 702.
 ——— thionyl-, i, 702.
β-Benzylhydroxylamine, nitroso-, the
 two isomeric benzyl derivatives of,
 i, 572.
 Benzylic alcohol, orthamido-, i, 21.
 ——— ——— action of carbon bi-
 sulphide on, i, 25.
 ——— ——— salts of, i, 20, 23.
 ——— ——— orthonitro-, i, 20.
 ——— ——— salts of, i, 20.
 ——— alcohols, azo- and hydrazo-, i, 201.
 ——— bisulphide, orthonitro-, i, 17.
 ——— chloride, action of aluminium
 chloride on, i, 561.
 ——— ——— melting point of, ii, 357.
 ——— ——— orthocyno- and orthonitro-,
 i, 16.
 ——— orthonitrophenylic ether, ortho-
 nitro-, i, 198.
 ——— silicate, i, 74.

- Benzyllic thiocyanate, orthamido-, i, 17.
 ——— onthonitro-, i, 17.
 Benzylidenecallylparatolylhydrazine,
 i, 704.
 Benzylidenecollidinedicarboxylic acid,
 i, 647.
 Benzylidenedeoxybenzoïn, i, 351, 352,
 353, 589.
 Benzylidenediacetamide, i, 713.
 Benzylidenediformamide, i, 712.
 Benzylidenedimethylbenzimidazole,
 i, 435.
l-Benzylidenementhylamine, i, 724.
n-Benzylidenementhylamine, i, 725.
 Benzylideneorthamidobenzyllic alcohol,
 i, 23.
 ——— metanitro-, i, 23.
 Benzylideneparamethoxycinchoninic
 acid, i, 729.
 Benzylideneparamidophenol, melting
 point of, i, 273.
 Benzylidenepernitronaphthylamine,
 TRANS., 1061.
 Benzylidenephénylpyrazolidine, i, 611.
 Benzylidenetolazone, i, 733.
 Benzylideneureide, metanitro-, i, 645.
 Benzylidenexylidine, i, 516.
 Benzylmalimides, i, 264.
 Benzylmetamidobenzoic acid, ortho-
 nitro-, i, 209.
 Benzylmetamidophenyl orthonitro-
 benzyl ether, orthonitro-, i, 198.
 Benzylmethylaminephenylsulphone,
 i, 204.
 Benzylmethylphenylbenzenylamidine,
 i, 205.
 Benzylorthotoluidine, ortho- and para-
 nitro-, i, 198.
 Benzylorthotoluylamide, orthamido- and
 orthonitro-, i, 50.
 Benzylparabromaniline, orthonitro-,
 i, 438.
 Benzylparatoluidine, orthamido-, i, 439.
 ——— paranitro-, i, 198.
 Benzylparatoluylamide, orthonitro-,
 i, 50.
 Benzylpentethylbenzene, i, 409.
μ-Benzylpenthiazoline, i, 427.
 Benzylphenanthridone, i, 722.
 Benzylphenylbenzenylamidine, i, 204.
 Benzylphenylbenzylthiourea, isomeric
 form of, TRANS., 538.
 Benzylphenylhydrazine, symmetrical;
 i, 371.
β-Benzylphenylhydrazine, i, 453.
 1-Benzylphthalazone, i, 348.
 Benzylphthalimide, orthonitro-, i, 415.
 ——— preparation of, i, 49.
 Benzylpropionamide, orthamido-, i, 51.
 ——— orthonitro-, i, 50.
 Benzylsuccinimide, orthonitro-, i, 415.
 Benzylthioethylphthalamic acid, i, 30.
o-Benzyltoluene, diamido-, i, 568.
 ——— nitramido-, and its derivatives,
 i, 567.
 4-Benzyl-1 : 2 : 6-triphenylpiazine di-
 hydride, TRANS., 1374.
 Bergapten, i, 342.
 ——— nitro-, i, 342.
 Beryl, phosphoric acid in, ii, 215.
 ——— preparation of glucina from,
 TRANS., 909.
 Beryllium ammonium fluoride, ii, 373.
 ——— experiments with wheat on the
 substitution for magnesium of,
 ii, 228.
 ——— oxide, preparation of, from beryl,
 TRANS., 909.
 ——— sulphite, basic, ii, 456.
 Betaine, action of alkalis on, i, 498.
 ——— occurrence of, in the sprouts of
 barley and wheat, i, 684.
 ——— occurrence of, in wormseed, ii, 485.
 Betelphenol, thermochemistry of, ii, 154.
 Beyrichite from Altenkirchen, ii, 18.
 Biacenaphthylidenediketone, i, 657.
 Biacridonyl, i, 650.
 Bidiphenylethylene, i, 38; PROC., 1892,
 192.
 Bile duct, influence of the ligature of, on
 metabolism, ii, 329.
 ——— estimation of cholic acid in, ii, 220.
 ——— of the ox, the acids of, ii, 220, 383.
 ——— pigments, chromic acid as a re-
 agent for, in urine, ii, 200.
 ——— detection of, in urine, ii, 398.
 Birch bark, products of the dry distilla-
 tion of, i, 130.
 Birds, urea in the blood of, ii, 581.
 Birotation of some sugars, i, 125.
 Bisdihydroxanthinic acid, i, 426.
 Bisdimethoxymetindolone, i, 372.
α-Bisdiphenylformamidylphenylhydr-
 azine and its derivatives, i, 461.
 Bismetindolone, i, 372.
 Bismuth, action of hydrochloric acid on,
 ii, 172.
 ——— ammonium chlorobromides,
 TRANS., 547.
 ——— fluoride, ii, 373.
 ——— detection of, ii, 192.
 ——— electrolytic estimation of, ii, 95.
 ——— electrolytic separation of, from
 cadmium, ii, 496.
 ——— electrolytic separation of, from
 cobalt, ii, 497.
 ——— electrolytic separation of, from
 cobalt, nickel, and zinc, ii, 497.
 ——— electrolytic separation of, from
 copper, ii, 495.
 ——— electrolytic separation of, from
 lead, ii, 495.
 ——— electrolytic separation of, from
 mercury, ii, 496.

- Bismuth, electrolytic separation of, from nickel, ii, 496.
 — gallate, basic, i, 643.
 — haloids, interaction of alkali haloids with, TRANS., 540.
 — iodide, solubility of, in methylenic iodide, ii, 378.
 — metallurgy of, ii, 534.
 — potassium chlorobromides, TRANS., 546.
 — pyrogallol, i, 644.
 — separation of arsenic from, ii, 186.
 — separation of silver from, ii, 493.
 — triacetyl-gallate, basic, i, 644.
 — sulphites, ii, 456.
 Bismuth-antimony-zinc alloys, ii, 522.
 Bismuth-cadmium-zinc alloys, ii, 522.
 Bismuth-silver-aluminium alloys, ii, 416.
 Bismuth-silver-zinc alloys, ii, 15.
 Bismuth-tin-aluminium alloys, ii, 415.
 Bismuth-tin-zinc alloys, ii, 15.
 Bitumen in the crystalline rocks of Sweden, ii, 326.
 Black-earth, analyses of, ii, 293.
 Blasting-gelatins, analysis of, ii, 196.
 Bleaching powder, constitution of, ii, 209, 277, 372.
 — — estimation of calcium chloride, chlorate, and hypochlorite in, ii, 388.
 — — specific gravity of solutions of, ii, 488.
 Blood, alkalinity of, during muscular work, ii, 218.
 — coagulation of, ii, 426.
 — composition of the small plates in, ii, 22.
 — defibrinated, influence of acids and alkalis on, ii, 332.
 — dextrose in, ii, 81.
 — diastatic action of the serum of, ii, 333.
 — diastatic ferment in, ii, 581.
 — gases of, during anæsthesia, ii, 540.
 — lactic acid in, ii, 136.
 — occurrence of glycogen in, ii, 176, 333, 541.
 — of birds, urea in the, ii, 581.
 — of certain mollusca, δ -achroglobin from, i, 615.
 — of Chitons, respiratory globulin in, i, 60.
 — of peptonised animals, gaseous tension in, ii, 131.
 — of worms, respiratory pigment in, i, 59.
 — precipitation of proteids from, preparatory to the estimation of sugar, ii, 398.
 Blood stains, chemico-legal examination of, ii, 312.
 Blood-corpuscles, action of physiological saline solution on, ii, 426.
 — — estimation of the volume of, ii, 331, 332.
 — — red, influence of acids and alkalis on the determination of the osmotic pressure in relation to, ii, 175.
 — — volume and amount of proteid in single, ii, 332.
 Blood-serum, conversion of starch into sugar by means of, ii, 187.
 Blow-pipe analysis, origin of, ii, 342.
 Blueite not a distinct species, ii, 535.
 Boiling point apparatus, Beckmann's, applications of, ii, 260.
 Boiling points of homologous compounds, PROC., 1893, 145.
 Bone, mucin in, ii, 134.
 Bone-black, estimation of iron and aluminium in, 498.
 Bone-meal, analysis of, ii, 389.
 Bones, fluorine in, ii, 81.
 Borates, action of sulphur and water on, ii, 205.
 Borax, manufacture of, ii, 460.
 — solution, normal, ii, 294.
 — use of, for standardising acids, ii, 232.
 Boric acid, estimation of, ii, 491.
 — — influence of, on the electrical conductivity of aqueous solutions of organic acids, ii, 506.
 Bornesitol, i, 295.
 Bornylic acetate, i, 660.
 — — occurrence of, in the ethereal oils of *Abies sibirica* and *A. pectinata*, i, 224.
 — butyrate, i, 660.
 — formate, i, 660.
 — propionate, i, 660.
 — valerate, i, 660.
 Boron, atomic refraction of, ii, 517.
 — atomic weight of, ii, 207; TRANS., 207.
 — bromide, combination of, with phosphorus bromides, ii, 518.
 — carbide, ii, 570.
 — estimation of, ii, 435.
 — phosphorus bromide, ii, 518.
 — presence of, in tomatoes, chick-peas, and *Iris germanica*, ii, 225, 227.
 — specific heat of, ii, 404.
 Brain, proteids of the, ii, 479.
 Brandite, ii, 420.
 Brassidic acid, constitution of, i, 551.
 — — oxidation of, i, 550.
 — — oxy-, i, 393.
 — — transformation of, into oleic and iso-oleic acids, i, 550.
 Brassylic acid, i, 306.
 Brazilin methyl ether, i, 225.

- Brazilite, ii, 286.
 Bread, digestibility of, ii, 24, 580.
 — estimation of fat in, ii, 197.
 — mouldy, changes in, ii, 545.
 — nutritive value of, ii, 24.
 Bright's disease, transformation of the albumin of the urine in, ii, 30.
 Bromal borneolates, i, 526.
 Bromine, atomic refraction of, ii, 254.
 — chlorine and iodine, detection of, in admixture, ii, 343.
 — — — separation and estimation of, ii, 42, 183, 295, 595.
 — estimation of, in mineral waters and mother liquors, ii, 595.
 — heat developed by the combination of, with unsaturated paraffinic compounds, ii, 444.
 — liquid, absorption of light by, ii, 561.
 — separation of iodine from, TRANS., 1051.
 Bromoborates, ii, 518.
 Bromoform, action of stannic chloride on, i, 121.
 — action of titanio chloride on, i, 121.
 Bronze, estimation of aluminium in, ii, 49, 243.
 Brushite, ii, 577.
 Bryogenin, i, 424.
 Bryonin, i, 424.
 Bryony root, active principle of, i, 424.
 Bryoresin, i, 424.
 Buildings, estimation of carbonic anhydride in the air of, ii, 240.
 Bulbocapnine, i, 492.
 Bunte's salt, i, 416.
 Burette for rapid titration, PROC., 1893, 182.
 Burner for light petroleum, ii, 368.
 — laboratory, ii, 368.
 Butallylmethylcarbinthionylamine, i, 702.
 Butane, secondary nitro-, i, 243.
 — tertiary nitro-, i, 243.
 Butanetetra-carboxylic acid, i, 253.
 Butenecarboxylic acid, pentachloro-, i, 698.
 $\alpha\gamma\delta$ -Butenyl- δ -hydroxytricarboxylic acid, lactone of, i, 176.
 Butidine, pentachloro-, i, 698.
 Butine, pentachloro-, i, 698.
 Butter, amount of lecithin in, ii, 543.
 — analysis of, ii, 602.
 — discrimination of, from margarin, ii, 603.
 — estimation of the insoluble fatty acids in, ii, 308.
 — estimation of volatile fatty acids in, ii, 197.
 — from cows variously fed, ii, 28.
 Butter production, relative value of maize, silage, and field and fodder maize for, ii, 141.
 — Reichert's process for, ii, 308.
 Butter-fat in milk, estimation of, ii, 252.
 — modification of the Reichert-Meissl method for, ii, 396.
 — sulphuric acid hydrolysis of, ii, 602.
 Butyl-alcoholic fermentation, ii, 586.
 Butylamine picrate, δ -bromo-, i, 9.
 — secondary, freezing points of aqueous solutions of, TRANS., 176.
 — tertiary, action of tertiary amyl iodide on, i, 128.
 — action of tertiary butylic iodide on, i, 128.
 Butylbenzene, tertiary, nitrazimido-, i, 637.
 — nitrodiamido-, i, 637.
 — triamido-, i, 636.
 Butylchloral, condensation of, with acetone and acetophenone, i, 302.
 Butylchloralacetophenone, i, 302.
 ψ -Butylethylene, i, 245.
 — glycol, i, 245.
 Butylic alcohol, normal, molecular weight of, in the liquid state, TRANS., 1102.
 — bromide, action of bromine on, i, 62.
 — chlorides, bromination of, i, 449.
 — glycerate, active normal, TRANS., 1411.
 — glycerates, active and inactive, TRANS., 516.
 — (secondary), active, TRANS., 519.
 — (tertiary), attempts to prepare, TRANS., 521.
 Butylideneacetophenone, trichloro-, i, 303.
o-Butylparaisopropyltoluene, i, 163.
p-Butylphenol, tertiary, derivatives of, i, 636.
 — dinitro-, i, 636.
 Butylphenylenemethenylamidine, nitro-tertiary-, i, 637.
 Butylphenylenemethenylamidine, nitrotertiary-, i, 637.
 Butyramide, α -isonitroso-, i, 503.
 Butyramidacetophenone, i, 531.
 Butyric acid, action of iodine on the silver salt of, i, 391.
 — α -amidoxyl, i, 502.
 — α -bromo- action of alcoholic potash on the anilide, toluidides, and naphthalides of, i, 51.
 — preparation of, i, 65.
 — α -isodibromo-, i, 134.
 — molecular weight in the liquid state, TRANS., 1103.

Butyric acid, solubility of the barium and calcium salts of, i, 547.
 Butyroanilide, *α*-bromo-, i, 52.
 Butyro-*α*-naphthalide, bromo-, i, 52.
 Butyro-*β*-naphthalide, *α*-bromo-, i, 52.
 Butyronitrile, *α*-amidoxy-, i, 502.
 Butyro-orthotoluidide, *α*-bromo-, i, 52.
 Butyroparatoluidide, *α*-bromo-, i, 52.
 Butyrylmalic acid, i, 501.
 — anhydride, i, 501.
l-Butyrylmenthylamine, i, 724.
γ-Butyrylmenthylamine, i, 725.
 Butyrylorthamidoacetophenone, i, 48.

C.

Cacao beans, estimation of theobromine in, ii, 198.
 Cadinene, i, 102, 103.
 Cadmium alkali sulphates, crystallography of, TRANS., 407.
 — ammonium fluoride, ii, 373.
 — atomic weight of, ii, 168.
 — detection of, ii, 192.
 — electrolytic estimation of, ii, 94, 191.
 — electrolytic separation of, from bismuth, ii, 496.
 — electrolytic separation of, from copper, ii, 306, 496.
 — fluoride, ii, 322.
 — glycerate, active and inactive, TRANS., 308.
 — haloïd salts of, action of, on piperidine and pyridine, i, 43.
 — phenylhydrazine sulphate, i, 268.
 — separation of arsenic from, ii, 186.
 — sulphite, ii, 277, 456.
 Cadmium-bismuth-zinc alloys, ii, 522.
 Cadmium-lead-zinc alloys, ii, 522.
 Cæsium arsenic haloïds, ii, 572.
 — aurobromide and aurochloride, ii, 68.
 — borate, ii, 460.
 — cadmium sulphates, crystallography of, TRANS., 410.
 — cobaltous sulphate, crystallography of, TRANS., 393.
 — copper sulphate, crystallography of, TRANS., 403.
 — ferrous sulphate, crystallography of, TRANS., 369.
 — flame spectrum of, ii, 402.
 — iodates, ii, 68.
 — lead bromides, ii, 322.
 — — chlorides, ii, 322.
 — — iodide, ii, 322.
 — magnesium sulphate, crystallography of, TRANS., 349.
 — manganous sulphate, crystallography of, TRANS., 376.

Cæsium mercury haloïds, ii, 69.
 — method of obtaining a persistent spectrum of, TRANS., 140.
 — nickelous sulphate, crystallography of, TRANS., 384.
 — pentahaloïds, ii, 68.
 — permanganate, ii, 325.
 — plumbichloride, ii, 523.
 — quantitative separation of, ii, 521.
 — salts, pure, preparation of, ii, 521.
 — silver chloride, ii, 69.
 — telluribromide, ii, 457.
 — tellurichloride, ii, 457.
 — telluriodide, ii, 457.
 — zinc sulphate, crystallography of, TRANS., 361.
 Caffeïne, action of iodine on, i, 375.
 — and coffee distillate, influence of, on metabolism, ii, 329.
 — and theïne, identity of, TRANS., 195.
 — and theobromine, separation of, ii, 608.
 — aurochloride, TRANS., 198.
 — bromo-, action of zinc ethide on, i, 376.
 — chloro-, action of potassium cyanide on, i, 376.
 — estimation of, ii, 559.
 — estimation of, in coffee, ii, 608.
 — estimation of, in tea, ii, 352, 608.
 — mercuric chloride, TRANS., 199.
 — potassium aurochloride, TRANS., 204.
 — reaction of, with auric chloride, TRANS., 195.
 — salts of, i, 489.
 Calcium and strontium nitrates, quantitative separation of, with amyl alcohol, ii, 241.
 — arsenates, ii, 274.
 — barium and strontium, separation of, ii, 436.
 — carbonate, action of dried hydrogen chloride on, ii, 208.
 — — fusion of, ii, 117, 166, 167.
 — — solubility of, ii, 520.
 — chloride, magnetic rotation of solutions of, ii, 442.
 — dextroethoxysuccinate, TRANS., 233.
 — distribution of, in nature, ii, 373.
 — estimation of, in basic slag, ii, 141.
 — flame spectrum of, ii, 402.
 — glycerate, active and inactive, TRANS., 297.
 — lævomethoxysuccinate, TRANS., 228.
 — magnesium, carbonic and sulphuric acids, distribution of acids and bases in a solution containing, TRANS., 697.

- Calcium, manganese, zinc, iron, and aluminium, separation of, ii, 600.
 — manganites, ii, 416.
 — methoxysuccinate, dextro-, TRANS., 335.
 — oxide, action of a high temperature on, ii, 167.
 — conditions of the absorption of carbonic anhydride by, TRANS., 822.
 — conditions of the absorption of sulphurous anhydride by, TRANS., 829.
 — inertness of, TRANS., 821.
 — volatilisation of, ii, 508.
 — oxychloride, ii, 276.
 — plumbate, dissociation of, ii, 524.
 — phosphate, soluble, reversion of, in soil, ii, 431.
 — volumetric estimation of, by means of uranium solution, ii, 301.
 — salts, absorption of, in the intestine, ii, 582.
 — separation of, from strontium, ii, 301.
 — separation of, from zinc, ii, 344.
 — sucates, i, 451.
 — sulphite, ii, 456.
 — solubility of, ii, 520.
 — from distillery residues, assay and purification of, ii, 558.
 — zincoxide, ii, 118.
- Calculus in muscle, ii, 334.
- Calves, full grown, deposition of albumin during the fattening of, ii, 25.
- Camphanamide, i, 526.
- Camphananilide, i, 526.
- Camphanic acid, action of water on, i, 524.
- Camphanmethylanide, i, 526.
- Camphanphenylhydrazide, i, 526.
- Camphelene, i, 109.
- Camphenaldehyde, i, 360.
- Camphene, action of phosphorus pentachloride on, PROC., 1893, 163.
- Camphenephosphonic acid, chloro-, PROC., 1893, 164.
- α -Camphenephosphonic acid, PROC., 1893, 164.
- β -Camphenephosphonic acid, PROC., 1893, 164.
- Camphenic acid, i, 361.
- Camphocarboxylic acid, i, 422.
- Campholamine, i, 108.
- Campholene, i, 109, 423.
 — dibromide, i, 423.
- Campholenic acid, derivatives of, i, 423.
- Campholenonitrile, i, 423.
- Campholylic alcohol, i, 109.
 — camphocarbamate, i, 108.
- Campholycamphelylcarbamide, i, 109.
- Campholytic acid, TRANS., 498.
- Campholytic acid dibromide, TRANS., 500.
- Camphor, amido-, i, 479.
 — and carvacrol, relation between, i, 524.
 — chloro-, PROC., 1893, 130.
 — action of zinc on, i, 524.
 — chlorobromo-, PROC., 1893, 130.
 — constitution of, i, 276, 422, 598.
 — constitution of the ketone obtained from, TRANS., 93.
 — β -dibromo-, action of phenylhydrazine on, i, 660.
 — oxidation of, i, 661.
 — dichloro-, PROC., 1893, 130.
 — formation of ketones by the action of sulphuric acid, zinc chloride, &c., on, TRANS., 75.
 — heat of combustion of, ii, 108.
 — isonitroso-, i, 660.
 — and its derivatives, i, 479.
 — nitroso-, conversion of, into camphoric imide, i, 277.
 — novel conversion of, into camphoric acid, i, 276.
 — propylamidophenol from, i, 152, 199.
 — sulphonation of, with anhydrosulphuric acid, TRANS., 549.
 — sulphonation of, with chlorosulphonic acid, TRANS., 552.
 — sulphonic derivatives of, TRANS., 548.
 — synthesis of an isomeride of, i, 419.
- Camphoramie acid, i, 479, 525.
- Camphorbenzylimide, i, 599.
- Camphorbenzylisoimide, i, 599.
- Camphor-derivatives, heats of combustion of, ii, 59.
- Camphordimethylamic acid, i, 525.
- Camphordimethyldiamide, i, 599.
- Camphordioximes, i, 277.
- Camphorethylisoimide, i, 599.
- Camphor-group, i, 660.
- Camphoric acid, i, 277.
 — action of phenylic isocyanate on, i, 361.
 — bromo-, action of amines on, i, 525.
 — constitution of, i, 600; TRANS., 506.
 — derivatives of, i, 524, 525.
 — ethereal salts of, i, 423.
 — function of, i, 361.
 — novel conversion of camphor into, i, 277.
 — oxidation of, i, 174.
 — salts of, i, 277.
 — substituted isoimides of, i, 599.
- Camphoric anhydride; action of phenylhydrazine on, i, 600.

- Camphoric anhydride, action of sodium ethoxide on, i, 362.
 ——— bromo-, i, 598.
 ——— bromo-derivatives of, i, 524.
 ——— fluorescein of, TRANS., 961.
 Camphoric imide, conversion of nitroso-camphor into, i, 277.
 Camphorisoimide, i, 599.
 Camphormethylamic acid, i, 525.
 Camphormethylimide, i, 599.
 Camphormethylisoimide, i, 599.
 Camphoroneoxime, i, 361.
 Camphoronephenylhydrazone, i, 361.
 Camphororthoquinone, i, 479.
 Camphors containing the group $\text{CO}\cdot\text{CH}_3$, i, 107.
 Camphorsulphonamide, inactive, TRANS., 570.
 ——— bromo-, TRANS., 583.
 ——— chloro-, TRANS., 598.
 ——— dextrorotatory, TRANS., 567.
 Camphorsulphonic acid and its salts, TRANS., 573.
 ——— bromo-, and its salts, TRANS., 584.
 ——— chloro-, and its salts, TRANS., 599.
 ——— chloride, TRANS., 551, 554.
 ——— action of heat on, PROC., 1893, 130.
 ——— bromo-, TRANS., 577.
 ——— chloro-, TRANS., 594.
 ——— dextrorotatory, isolation of, TRANS., 554.
 ——— laevorotatory, probable existence of, TRANS., 557.
 Camphothetic acid, TRANS., 504.
 Camphren, oxidation of, TRANS., 96, 97.
 ——— preparation of, TRANS., 77.
 Camphylic acid, sulpho-, i, 363; PROC., 1893, 109.
 ——— distillation of, PROC., 1893, 109.
 ——— oxidation of, PROC., 1893, 110.
 Cane-sugar, benzoate from, i, 186.
 ——— "spontaneous" inversion of, i, 547.
 Cantharic acid, hydrazide of, i, 40.
 Cantharidin, action of ethylenediamine on, i, 483.
 ——— action of orthophenylenediamine on, i, 483.
 ——— action of orthotoluylenediamine on, i, 484.
 ——— action of phenylhydrazine on, i, 40, 278.
 ——— constitution of, i, 278.
 ——— derivatives of, i, 483.
 ——— hydrazone, dinitro-, i, 483.
 ——— preparation of, i, 600.
 Cantharidin, reduction of, i, 483.
 Cantharidinphenylhydrazone hydrate, i, 40.
 ——— reactions of, i, 278.
 Caoutchouc, absorption of sulphurous anhydride by, ii, 564.
 ——— membranes, diffusibility of certain gases through, ii, 564.
 Capillary separation of substances in solution, PROC., 1893, 123.
 Caproic acid, action of iodine on the silver salt of, i, 391.
 ——— action of phosphoric anhydride on, TRANS., 460.
 ——— α -amidoxyl, i, 503.
 ——— normal, preparation of, i, 687.
 Caprylamide, α -isonitroso-, i, 503.
 Caprylic acid, α -amidoxyl-, i, 503.
 Caprylic iodide, secondary, action of, on trimethylamine, i, 7.
 Caprylone oxime, TRANS., 454.
 ——— preparation of, TRANS., 453.
 Caprylonitrile, α -amidoxyl, i, 503.
 Capsicum, composition of the ripe husks of, ii, 546.
 Caramel, cryoscopy of, i, 619.
 ——— formation of hydrocyanic acid by the action of nitric acid on, i, 617.
 ——— molecular formula of, i, 619.
 Carbamic acid in the urine after ingestion of lime, ii, 333.
 Carbamide amidoacetate, thermochemistry of, ii, 696.
 ——— preparation of, i, 696.
 ——— thermochemistry of, ii, 358.
 ——— See also Urea.
 Carbanilide, hexanitro-, TRANS., 1064, 1068.
 Carbanilidocuminantialdoxime, i, 708.
 Carbanilidometanitrobenzantialdoxime, i, 708.
 Carbanilido-orthonitrobenzantialdoxime, i, 708.
 Carbanilido-orthonitrobenzsynaldoxime, i, 710.
 Carbanilidoparamethoxybenzantialdoxime, i, 707.
 Carbanilidoparamethoxybenzsynaldoxime, i, 707.
 Carbazacridine, i, 417.
 Carbazides, thiosemi-, stereoisomeric, i, 26.
 Carbazole, i, 349.
 ——— bromonitro-, i, 349.
 ——— conversion of, into indole, i, 717.
 ——— formation of, from tetrazodiphenyl, i, 588.
 Carbodiimides, molecular weight of, i, 701.
 Carbodiparatolylimides, molecular weights of, i, 701.
 Carbodiphenylimide, Wessel's dicarbo-

- base from phenylhydrazine and, i, 461.
- Carbohydrates, formation of benzoates from, i, 186.
- heats of combustion of, ii, 59.
- in leguminous seeds, ii, 139.
- of normal urine, ii, 542.
- of the coffee berry, ii, 84.
- of the Jerusalem artichoke, i, 617.
- recent investigations on, i, 547.
- urinary, relation of, to humous substance, ii, 82.
- Carbolic acid, crude, estimation of phenols in, ii, 394.
- Carbon and nitrogen, simultaneous estimation of, in organic compounds, ii, 501.
- atomic refraction of, ii, 254.
- atomic weight of, ii, 165.
- bisulphide, action of aqua regia on, ii, 571.
- — depression of the freezing point of acetic acid by, TRANS., 1025.
- — depression of the freezing point of benzene by, TRANS., 1022.
- — molecular weight of, in the liquid state, TRANS., 1099.
- combustion of, in air, ii, 461.
- cyclic condensation of, ii, 519.
- estimation of, in iron and steel, ii, 45, 491.
- oxychloride, preparation of, from carbon tetrachloride, i, 681.
- preparation of, under high pressure, ii, 275.
- tetrabromide, action of stannic chloride on, i, 121.
- tetrachloride, action of hydriodic acid on, i, 1.
- — molecular weight of, in the liquid state, TRANS., 1099.
- trichloriodide, i, 185.
- volatilisation of, in the electric arc, ii, 408.
- Carbonado in blue earth from the Cape, ii, 285.
- Carbonates, action of sulphur and water on, ii, 205.
- hydrogen alkali, analysis of, ii, 190.
- Carbonic acid, estimation of, in aqueous solutions, ii, 45.
- — sulphuric acid, calcium and magnesium, distribution of acids and bases in a solution containing, TRANS., 696.
- Carbonic anhydride, amount of, in the air, ii, 67.
- — and methylic chloride, measurement of Van der Waals' surface for mixtures of, ii, 260.
- — and oxygen, exchange of, between plants and the atmosphere, ii, 180.
- Carbonic anhydride, assimilation of, by chlorophyllous plants, ii, 483.
- — condensation of, under the influence of sun-light, ii, 484.
- — condition of the absorption of, by calcium oxide, TRANS., 822.
- — diffusion of, in water, ii, 62.
- — estimation of, in the air of buildings, ii, 240.
- — in the air of soils, influence of the pressure of, on vegetation, ii, 341.
- — influence of, on the diastatic and peptone-forming ferments in the organism, ii, 475.
- — specific heat of, ii, 5.
- Carbonic oxide, action of, on potassium ammonium and sodammonium, ii, 520.
- — action of, on reduced hæmatin and hæmochromogen, i, 448.
- — and oxygen, ignition point of a mixture of, ii, 258.
- — density of, ii, 165.
- — elimination of, ii, 131, 288.
- — formation of, in gas producers, ii, 461.
- — heat of combustion of, ii, 444.
- Carboparatoluidocuminantialdoxime, i, 708.
- Carboparatoluidocuminsynaldoxime, i, 708.
- Carboparatoluidometanitrobenzantialdoxime, i, 709.
- Carboparatoluidometanitrobenzsynaldoxime, i, 709.
- Carboparatoluidoorthomethoxybenzantialdoxime, i, 708.
- Carboparatoluidoorthonitrobenzantialdoxime, i, 709.
- Carboparatoluidoorthonitrobenzsynaldoxime, i, 710.
- Carboparatoluidoparamethoxybenzantialdoxime, i, 707.
- Carboparatoluidoparamethoxybenzsynaldoxime, i, 707.
- Carboparatoluidoparanitrobenzantialdoxime, i, 708.
- Carboparatoluidoparanitrobenzsynaldoxime, i, 708.
- Carbophenyldiimide, molecular weight of, 701.
- Carborthotoluidocuminantialdoxime, i, 708.
- Carborthotoluidometanitrobenzantialdoxime, i, 708.
- Carborthotoluidoorthomethoxybenzantialdoxime, i, 708.
- Carborthotoluidoparamethoxybenzantialdoxime, i, 707.
- Carborthotoluidoparamethoxybenzsynaldoxime, i, 707.
- Carborthotoluidoparanitrobenzantialdoxime, i, 708.

- Carborthotoluidoparanitrobenzsynald-oxime, i, 708.
 Carboxydehydracetic acid, i, 398.
 ——— hydrazide of, i, 400.
 Carboxydehydropropionylacetic acid, i, 399.
 Carboxyl group, influence of, on the toxic action of aromatic compounds, ii, 178.
 Carboxyphenylglyoxylic acid [1:2], i, 476.
Carica papaya, alkaloïd from the leaves of, i, 740.
 Carotene, detection of in plants, ii, 33.
 ——— from pollen, ii, 139.
 Carpaïne, i, 740.
 ——— nitroso-, i, 741.
 Carvacrol and camphor, relation between, i, 524.
 Carvacrylamine, i, 723.
 Carvole, i, 723.
 Carvomenthene, i, 359.
 Carvomenthol, tertiary, i, 723.
 Carvomenthylamine, tertiary, i, 723.
 Carvomenthylphenylthiocarbamide, i, 723.
 γ -Carvoxime, reduction of, i, 723.
 α -Carvylamine, i, 723.
 β -Carvylamine salts, i, 723.
 α -Carvylphenylcarbamide, i, 723.
 β -Carvylphenylcarbamide, i, 723.
 Caryophyllene alcohol and its derivatives, i, 101.
 Cascarin, identity of, with rhamno-xanthin, i, 113.
 Casein solutions, filtration of, through porcelain, i, 540.
 Casava, products of, ii, 430.
 Catechol, action of chlorine on, i, 698.
 ——— action of light on, i, 642.
 ——— action of sulphuric acid on, i, 637.
 ——— azo-derivatives of, i, 410.
 ——— diamido-, i, 699.
 ——— dinitro-, and its conversion into nitranilic acid, i, 699.
 Catecholdiazobenzenesulphonic acid, i, 410.
 Catecholdisulphonic acid, i, 638.
 Catecholsulphonic acid, i, 637.
 Cell, a one-volt standard, ii, 562.
 ——— Clark, as a standard of electro-tive force, ii, 107.
 ——— Planté, chemistry of, ii, 3, 4.
 Cells, detection of phosphorus in, ii, 135.
 ——— green plant, assimilation of formaldehyde by, ii, 32.
 ——— oxidation, electromotive force of, ii, 58.
 ——— vegetable, supposed presence of albumin in the walls of, ii, 180.
 ——— voltaic, with fused electrolytes, ii, 403.
 Cellulose, action of dilute acids and alkalis on, i, 127.
 ——— alkali, and carbon bisulphide, interaction of, TRANS., 837.
 ——— animal, i, 497.
 ——— benzoates, TRANS., 838.
 ——— constitution of, TRANS., 843.
 ——— inversion of, i, 249.
 ——— nitrate, estimation of nitrogen in, ii, 184.
 ——— nutritive value of, ii, 22.
 ——— oxy-, i, 387.
 ——— regenerated, TRANS., 840.
 ——— thiocarbonates, TRANS., 837.
 Cellulosethiosulphocarbonic acid, TRANS., 839.
 Cephalantein, i, 113.
 Cephalantin, i, 112.
Cephalanthus tannin, i, 113.
 Cerberetin, i, 482.
 Cerberin, i, 481.
 Cerebrin, i, 235.
 Cerebrosides of the medullary sheath of nerve fibres, i, 234.
 Cerium chloride, anhydrous, ii, 466.
 Cerium-group, separation of the metals of, ii, 283.
 Cerotolic acid, i, 59.
Cetraria nivalis, analysis of, ii, 593.
 Cevadine, i, 490.
 Chalybite, cobaltiferous, from Neunkirchen, ii, 129.
 Champacol, i, 480.
 Charcoal, behaviour of, with halogens, nitrogen, sulphur, and oxygen, ii, 571.
 ——— formation of hydrocyanic acid by the action of nitric acid on, i, 617.
 Chay root, colouring and other principles contained in, TRANS., 1160.
 Chebulic acid, i, 212.
 Cheese, over-ripe, composition of, ii, 29.
 Chelerythrine, i, 490.
 Chemical action at very low temperatures, ii, 112.
 ——— influence of moisture in promoting, ii, 462; PROC., 1893, 129.
 ——— change, conditions determinative of, PROC., 1893, 145.
 ——— changes, conservation of mass in, ii, 452.
 ——— energy, transformation of, into electrical energy, ii, 107.
 ——— theory, attempt to found a, on a basis of physical comparison, ii, 10.
 ——— types, theory of, ii, 408.
 ——— union, method of measuring loss of energy due to, ii, 63.
 Cherry tree gum, organised ferment from, ii, 180.
 Chesnut bark tannin, i, 343.
 Chick-peas, composition of, ii, 226.

- Chick-peas, presence of boron, copper, and lithium in, ii, 226.
- Child 14 months old, metabolism in, ii, 476.
- Chitin, i, 288.
- Chitins, i, 614.
- Chitons, respiratory globulin in the blood of, i, 60.
- Chloral, action of, on benzene, i, 718.
- condensation of ketones with, i, 389.
- condensation of, with acetone and acetophenone, i, 302.
- derivatives of, i, 301.
- hydrate, influence of, on metabolism, ii, 543.
- molecular weight of, in the liquid state, TRANS., 1100.
- Chloralacetone, i, 302, 390.
- dibromo-, i, 390.
- Chloralacetophenone, i, 302, 390.
- Chloral-ammonia, i, 301.
- Chloralantipyrine, i, 301.
- Chloraldiformamide, i, 301.
- Chloralose and its physiological properties, i, 247.
- Chloramines, i, 497.
- Chloranil, derivatives of, i, 322.
- Chlorates, action of sulphurous anhydride on, ii, 115.
- and nitrates, estimation of, in one operation, ii, 596.
- chlorides and hypochlorites, estimation of admixed, ii, 388.
- Chloreserine, i, 741.
- Chlorides, hypochlorites, and chlorates, estimation of admixed, ii, 388.
- metallic, action of liquid chlorine on, ii, 464.
- source of error in the volumetric estimation of, by Mohr's method, ii, 433.
- Chlorine, action of, on charcoal, ii, 571.
- and hydrogen, ignition point of a mixture of, ii, 258.
- and mercury, interaction of, PROC., 1893, 38.
- atomic refraction of, ii, 254.
- bromine and iodine, detection of, in admixture, ii, 343.
- — separation and estimation of, ii, 183, 295, 595.
- density and molecular volume of, ii, 410.
- estimation of, in electrolysed solutions, ii, 41.
- estimation of, in water, ii, 550.
- estimation of, in wine, ii, 233.
- free, volumetric estimation of, ii, 488.
- separation of iodine from, ii, 183; TRANS., 1051.
- Chlorite-group, ii, 19.
- Chlorites, constitution of, ii, 78.
- Chloroborates, preparation of, ii, 468.
- "Chlorocodide," i, 675.
- Chloroform, decomposition of, in presence of iodine, i, 242.
- m. p. of, ii, 357.
- oxidation of, with chromic acid, i, 681.
- pure, preparation of, i, 121.
- Chlorophyll, i, 41.
- alkaline, i, 41.
- Chlorosis, ii, 541.
- iron in, ii, 427.
- Cholera, excretion of ethereal hydrogen sulphates in, ii, 290.
- Cholesterol, estimation of, ii, 310.
- Cholic acid, estimation of, in bile, ii, 220.
- Choline nitrite, i, 298.
- occurrence of, in the sprouts of barley and wheat, i, 684.
- occurrence of, in wormseed, ii, 485.
- Chondrostibian, ii, 577.
- Chromammonium compounds, thiocyanates of, i, 290.
- Chromates, action of sulphur and water on, ii, 205.
- Chromatin, demonstration of the presence of iron in, ii, 24.
- Chrome alum, dissociation of, ii, 73.
- alums, anhydrous, ii, 573.
- Chrome-iron-ore from Lower Silesia, ii, 178.
- Chromium ammonium sulphate, ii, 572.
- chloride, action of ammonia on, at low temperatures, ii, 469.
- chlorides, violet and green, cryoscopic behaviour of aqueous solutions, ii, 122.
- crystalline form of, ii, 281.
- detection of, in presence of iron and manganese, TRANS., 1082.
- electrolytic preparation of, ii, 122.
- estimation of, by aid of sodium peroxide, TRANS., 1081.
- estimation of, in steel, &c., ii, 554.
- fluoride, ii, 282.
- oxalates, absorption spectra of, ii, 314.
- oxide, action of a high temperature on, ii, 167.
- potassium sulphate, ii, 573.
- preparation of, ii, 281.
- sulphites, ii, 456.
- tungstate, crystalline, ii, 574.
- volumetric estimation of, ii, 194.
- Chromium-compounds, absorption spectra of, ii, 313.
- Chromodisulphuric acid, ii, 470.
- Chromopyrosulphuric acid, ii, 528.
- Chromosulphochromic acid, ii, 470.
- Chromotrisulphuric acid, ii, 470.

- Chromous fluoride, ii, 281.
 Chrysene, i, 593.
 Chrysenic acid, constitution of, i, 594.
 ——— distillation of, with lime, i, 593.
 Chrysoïdine, action of formaldehyde on, i, 574.
 ——— thionyl-, i, 518.
 Chrysomethylpiazine, TRANS., 1292.
 Chrysopiazine, TRANS., 1290.
 ——— 1 : 4-dihydride, TRANS., 1289.
Cicer arietinum, composition of, ii, 226.
Cicuta virosa, ethereal oil of the seeds of, i, 634.
 Cinchona alkaloïds, i, 181.
 ——— conversion of, into isomerides, i, 56.
 ——— new isomerides of the ethiodides of, i, 738.
 ——— bark, estimation of quinine in, ii, 200, 310.
 Cinchonamine, physiological action of, ii, 223.
 Cinchonibine, i, 679.
 Cinchonic acid, i, 114.
 ——— acids, alkyl- and alkylene-derivatives of, i, 728.
 Cinchonine, i, 677.
 ——— conversion of, into isomerides, i, 56.
 ——— dihydrochloride, i, 677.
 ——— ethiodide, isomeride of, i, 738.
 ——— hydrochloro-, i, 678.
 ——— molecular transformation of, i, 181.
 ——— solutions, rotatory power of, ii, 106.
 β -Cinchonine, i, 56, 181.
 γ -Cinchonine, i, 56.
 Cinchonidine, i, 676.
 ——— action of hydriodic acid on, i, 231.
 ——— conversion of, into isomerides, i, 56.
 ——— ethiodide, isomeride of, i, 738.
 β -Cinchonidine, i, 56, 232.
 γ -Cinchonidine, i, 56, 232.
 Cineole, detection of, in ethereal oils, ii, 395.
 Cinnamaldiureide, i, 646.
 Cinnamaleureide, i, 646.
 Cinnamene, action of nitrosyl chloride on, TRANS., 483.
 ——— hydrochloride and hydrobromide, i, 562.
 Cinnamic acid, allo-, new synthesis of, i, 513.
 ——— condensation of, with hydrocarbons, i, 512.
 ——— dibromide, separation of, into its optically active components, i, 582.
 ——— dibromides, optically active, i, 414.
 Cinnamic acid, dichlorides, optically active, i, 415.
 ——— diiodo-, action of water and heat on, i, 19.
 Cinnamylamidoacetophenone, i, 532.
 Cinnamylamine and its derivatives, i, 568.
 Cinnamylbenzamide, i, 569.
 Cinnamylcocaine, derivatives of, i, 57.
 Cinnamylidene, i, 703.
 Cinnamylideneallylparatolyhydrazine, i, 704.
 Cinnamylideneparamidophenol, m. p. of, i, 273.
 Cinnamylphenylthiocarbamide, i, 569.
 Cinnamylphenyl- ψ -thiocarbamide, i, 569.
 Cinnamylphthalamic acid, i, 569.
 Cinnamylphthalimide, i, 568.
 ——— dibromides, i, 569.
 Citraconfluoresceïn, TRANS., 677.
 ——— action of bromine on, TRANS., 682.
 ——— derivatives of, TRANS., 677.
 ——— dinitro-, TRANS., 683.
 Citraconic acids, conversion of, into mesaconic acids, i, 190.
 Citrates, action of sulphur and water on, ii, 205.
 Citrazinamide, preparation of, TRANS., 1036.
 Citrazinic acid, TRANS., 1035.
 ——— action of nitrous acid on, TRANS., 1043.
 ——— alkali salts of, TRANS., 1040.
 ——— isonitroso-, TRANS., 1047.
 ——— tribromo-, TRANS., 1042.
 ——— trichloro-, TRANS., 1041.
 Citrazinimide, alkali salts of, TRANS., 1039.
 Citrene, action of sulphuric acid on, i, 223.
 Citric acid, detection and estimation of lead in, ii, 599.
 ——— estimation of, in wine, ii, 54.
 ——— examination of, for lead, ii, 557.
 ——— formation of, by the fermentation of glucose, ii, 591.
 Citronellaldehyde, i, 685.
 ——— nitrile of, i, 685.
 Citronellaldoxime, i, 685.
 Citronellapimelic acid, i, 685.
 Citronellalic acid, i, 685.
Cladonia rangiferina, analysis of, ii, 593.
 Clark cell as a standard of electromotive force, ii, 107.
 Clay, estimation of silica in, ii, 300.
 ——— estimation of, in soils, ii, 97.
 ——— filters, ii, 368.
 Clinchlore, constitution of, ii, 78.
 Clinton iron-ore, ii, 76.

- Clovene, i, 102.
 Cloves, oil of, detection of, ii, 397.
 Coagulation, fractional heat, of proteïds, i, 59.
 — intravascular, ii, 541.
 — of blood, ii, 426.
 Coal, estimation of sulphur in, ii, 89, 187.
 Coal-gas, estimation of nitrogen in, ii, 296.
 Coal-tar colouring matters, qualitative analysis of, ii, 610.
 Cobalt, action of strong aqueous potash on, ii, 468.
 — and nickel, separation of, by means of nitroso- β -naphthol, ii, 500.
 — atomic weight of, ii, 469, 574.
 — electrolytic estimation of, ii, 94, 192.
 — electrolytic separation of bismuth from, ii, 497.
 — electrolytic separation of copper from, ii, 496.
 — elementary nature of, ii, 469.
 — oxide, action of a high temperature on, ii, 167.
 — question as to the homogeneous nature of, ii, 212.
 — separation of manganese from, TRANS., 1082.
 — sulphites, ii, 456.
 — volumetric estimation of, ii, 194.
 Cobaltammonium salts, electrical conductivity and constitution of, ii, 507.
 Cobaltiferous chalybite from Neunkirchen, ii, 129.
 — iron pyrites from Müsen, ii, 18.
 Cobaltous alkali sulphates, crystallography of, TRANS., 388.
 Coca leaves, i, 57, 182.
 β -Cocaïc acid, i, 58.
 Cocaine and ecgonine, separation of, ii, 609.
 — estimation of, ii, 609.
 — hydrochloride, melting point of, i, 738.
 — physiological action of, ii, 334.
 Cochineal, detection of, in sausages, ii, 56.
Cochlearia armoracia, essential oil of, i, 633.
 Cocoa preparations, estimation of sugar in, ii, 100.
 Cod-liver oil, alkaloïds of, ii, 290.
 Codeïne, amorphous, identity of, with pseudocodeïne, i, 675.
 — salts, i, 675.
 Codide, chloro-, i, 675.
 — sulpho-, i, 676.
 Coffee, estimation of caffèïne in, ii, 608.
 — influence of, on artificial digestion, ii, 540,
 Coffee-berry, carbohydrates of the, ii, 84.
 Cohesion of elements and compounds, ii, 155.
 Collidine, new, i, 175.
 Colloïd, ii, 218.
 Colloïds, behaviour of, in organic solvents, at the critical temperature thereof, ii, 259.
 Colophony, terpenes from, i, 100.
 Colour, change of, as indicative of change of structure, PROC., 1893, 55.
 — of solutions of salts in water, influence of the concentration of the ions on, ii, 203.
 — origin of, TRANS., 243; PROC., 1892, 189, 194; 1893, 52, 55, 93.
 Colouring matters, coal-tar, qualitative analysis of, ii, 610.
 — principles of chay root, TRANS., 1160.
 — of morinda root, TRANS., 1184.
 — of *Rubia sikkimensis*, TRANS., 1157.
 — of wong-koudu, TRANS., 1185.
 Coma, diabetic, ii, 543.
 Combustion by oxygen, ii, 412.
 — point, ii, 202, 257, 258.
 Conchinine, hydrochloro-, i, 677.
 Conductivity of electrolytes in various solvents, ii, 151.
 Congo-red, action of formaldehyde on, i, 574.
 Conifer, isolation of, from *Scorzonera hispanica*, i, 110.
 Coniine, a homologue of, i, 442.
 — and nicotine, discrimination and separation of, ii, 607.
Convolvulus panduratus, glucoside of, i, 472.
 — *scammonia*, glucoside of, i, 423.
 Cookeite from Paris and Hebron, Maine, ii, 538.
 Copal resin, terpenes from, i, 100.
 Copper acetate, compounds of, with ammonia and pyridine, i, 131.
 — action of nitric acid on, ii, 272.
 — alkali sulphates, crystallography of, TRANS., 396.
 — ammonium fluoride, ii, 373.
 — and antimony, simultaneous precipitation of, by the galvanic current, ii, 72.
 — antimony, and tin, analysis of alloys of, ii, 242.
 — arsenates, ii, 274.
 — atomic weight of, ii, 12.
 — detection of, ii, 192.
 — electrolytic estimation of, ii, 93, 191.

- Copper, electrolytic separation of, from antimony, ii, 495.
 — electrolytic separation of, from bismuth, ii, 495.
 — electrolytic separation of, from cadmium, ii, 306, 496.
 — electrolytic separation of, from iron and zinc, ii, 496.
 — electrolytic separation of, from mercury, ii, 305.
 — electrolytic separation of, from nickel, ii, 306, 496.
 — electrolytic separation of, from silver, ii, 305.
 — electrolytic separation of, from zinc, ii, 496.
 — electrolytic separation of, from zinc, nickel, and cobalt, ii, 496.
 — estimation of, ii, 493.
 — estimation of, by Volhard's thiocyanate method, ii, 345.
 — estimation of, in alloys, ii, 95.
 — ethoxide, i, 686.
 — fluorides, ii, 525.
 — fusion and volatilisation of, in the electric arc, ii, 508.
 — graphochemistry of, ii, 278.
 — hydroxide, action of haloïd salts on, ii, 210.
 — — and its basic salts, dehydration of, ii, 374.
 — — dehydration of, in presence of water, ii, 210.
 — lead, tin, and antimony, separation of, ii, 95.
 — lithium chloride, ii, 119.
 — nitro-, ii, 374.
 — oxide, action of a high temperature on, ii, 167.
 — oxybromide analogous to atacamite, ii, 463.
 — possible volatility of, below its melting point, ii, 168.
 — potassium fluoride, ii, 373.
 — presence of, in tomatoes, chick peas, and *Iris germanica*, ii, 225—227.
 — pyruvate, i, 686.
 — rubidium fluoride, ii, 373.
 — salts, a reaction of, ii, 554.
 — — absorption spectra of, in solution, ii, 149.
 — sulphates, basic, new formation of, ii, 169.
 — sulphite, basic, ii, 456.
 — volumetric estimation of, ii, 492.
 — See also Cuprous.
 Coriander, essence of, i, 661.
 Coriandrol, i, 661.
 Cork, constituents of, ii, 181.
 Corresponding states, Van der Waals', ii, 63.
- Corundum, alteration of, ii, 421.
 Corycavine, i, 492.
 Corydaline, i, 492.
 Corydaliobiline, i, 446.
Corydalis cava, alkaloïds from, i, 492.
 — — new alkaloïd from, TRANS., 485.
 — — *nobilis*, alkaloïds of, i, 446.
 Corydine, i, 492.
 Corytuberine, TRANS., 486.
 — methiodide, TRANS., 487.
 — salts, TRANS., 486.
 Cotinine, i, 287, 444.
 — dibromo-, and its derivatives, i, 286.
 Cotogenin, i, 417.
 Cotton, absorption of mercuric chloride from dilute solutions by, i, 387.
 Cotton-seed meal, available phosphoric acid and soluble potash in, ii, 594.
 — — oil, detection and approximate estimation of, in lard and olive oil, ii, 440.
 — — — heated, detection of, in lard, ii, 603.
 Coumalin rings, formation of, i, 403.
 Coumalinic acid, i, 401.
 Coumarone derivatives, synthesis of, i, 254.
 Cows, feeding experiments on, with sunflower cake, ii, 328.
 — milk of different breeds of, ii, 220.
 — — variously fed, butter from, ii, 28.
 Cream of tartar, solubility of, in dilute alcohol, i, 308.
 Creatinine, sarcous, and its salts, i, 55.
 Creosotes, analysis of, ii, 307.
 — composition of, i, 320.
 Cresol, diamido-, i, 566.
 o-Cresol, supposed formation of, from 1 : 2 : 5-methylsalicylic acid, i, 563.
 Cresolglycollamides, i, 269.
 Cresolglycollic acids, derivatives of, i, 269.
 o-Cresolphthaleïnoxime, i, 719.
 Cresotic acid, amido-, i, 567.
 — — bromo-, i, 57.
 — — chloro-, i, 567.
 — — iodo-, i, 567.
 — anhydride, ortho-, 217.
 ε-p-Cresoxyamylamine, i, 10.
 δ-p-Cresoxyvaleric acid, i, 10.
 δ-p-Cresoxyvaleronitrile, i, 10.
 p-Cresylic phthalate, i, 275.
 — titanate, i, 257.
 Critical constants of certain ethereal salts, TRANS., 1191, 1243, 1257.
 — — of organic compounds, ii, 446.
 — — point, determination of molecular weight at the, ii, 204.

- Critical point, effect of gravity on fluids at the, ii, 112.
 — points, Cailletet and Colardeau's method of determining, ii, 111.
 — temperatures, new method of calculating, TRANS., 1107.
 Crotonic acid, chlorination and bromination of, i, 132.
 — — diiodo-, i, 397.
 — — solid, addition of bromine and chlorine to, i, 134.
 — acids and their derivatives, i, 132.
 — — β -chloro-, oxidation of, i, 549.
 — — solid, formation of, by the reduction of α -isobromo- and α -isochloro-crotonic acids, i, 134.
 Crotonylene diiodide, i, 2.
 — preparation of, i, 2.
 Crucible, Gooch, use of the, ii, 90.
 Cryohydric quintuple points, ii, 447.
 — temperatures, ii, 512.
 Cryoscopic behaviour of acetates of feeble bases, i, 667.
 — — of weak solutions, ii, 110.
 — determinations, phenanthrene as a solvent in, ii, 512.
 — method, more exact, ii, 261.
 — studies in the benzene series, i, 270.
 Cryoscopy of ammoniometallic compounds, ii, 156.
 α -Crystallin, ii, 424.
 β -Crystallin, ii, 425.
 Crystallography of the potassium, rubidium, and caesium salts of the monoclinic series of double sulphates, $R_2M(SO_4)_2 \cdot 6H_2O$, TRANS., 337.
 Crystals of isomorphous series, connection between the atomic weight of contained metals and the magnitude of the angles of, TRANS., 337.
 Cumazone, thio-, i, 25.
 ψ -Cumene, behaviour of halogen derivatives of, towards sulphuric acid, 1, 408.
 — dinitrofluoro-, i, 408.
 — fluoripdo-, i, 408.
 — fluorodibromo-, i, 408.
 — fluorodichloro-, i, 408.
 — nitrofluoro-, i, 408.
 ψ -Cumeresulphonic acid, fluoro-, i, 408.
 — — fluorobromo-, i, 408.
 — — fluorochloro-, i, 408.
 Cumidine, thionyl-, i, 517.
 ψ -Cumidine, fluoro-, i, 408.
 — thionyl-, i, 517.
 Cuminaldiureide, i, 646.
 Cuminaldoximes, action of phenylhydrazine on, i, 87.
 ψ -Cumylic phthalate, i, 275.
 Cupreine and its derivatives, physiological action of, ii, 223.
 Cuproidargyrite, ii, 285.
 Cuproplumbite from Butte City, Montana, ii, 286.
 Cuprous cyanide, combination of, with alkali cyanides, i, 289.
 — fluoride, non-existence of, ii, 125.
 — mercuric iodide, ii, 554.
 — phosphide, ii, 526.
 Cyanacetamide, thio-, i, 405.
 Cyanacetic acid, condensation of fatty aldehydes with, i, 455.
 Cyanacetone hydrazone, i, 315, 571.
 Cyanacetophenone hydrazone, i, 315.
 o-Cyanacetophenonecarboxylic acid, i, 468.
 Cyanacetoxime, i, 314.
 Cyanides, condensation of, with ethereal salts, i, 396.
 o-Cyanobenzenesulphonamide, i, 715.
 o-Cyanobenzenesulphonic acid, i, 715.
 o-Cyanobenzoic acid, i, 268.
 Cyanocrotonic acid, i, 455.
 o-Cyanodiphenylmethane, i, 16.
 Cyanofumaric acid, i, 455.
 Cyanogen, decomposition of, in acid, alkaline, and aqueous solutions, i, 541.
 — detection and estimation of, in iodine, ii, 246.
 — estimation of, in coal-gas, ii, 51.
 — estimation of, in the spent materials from gas purifiers, ii, 50.
 — iodide, action of sodium thiosulphate on, ii, 246.
 — — volumetric estimation of, ii, 245.
 — radicle, mechanical comparison between the halogens and, i, 1.
 Cyanomalonic acid, i, 455.
 o-Cyanophenyltolylmethane, i, 17.
 Cyanotrimethyldihydro-2-pyridone, i, 484.
 Cycloid systems, constitution of, i, 603.
 Cymene, critical constants of, ii, 446.
 — magnetic rotation of, ii, 442.
 — optically inactive, preparation of, from oil of caraway, i, 17.
 m-Cymene, i, 597.
 Cymidine [1 : 3 : 4], conversion of tanacetoxime into, i, 78.
 m-Cymyl methyl ketone, i, 163.
 o-Cymyl ethyl ketone, i, 465.
 — — ketoxime, i, 465.
 — propyl ketone, i, 465.
 — — ketoxime, i, 465.
 o-Cymylacetamide, i, 465.
 m-Cymylcarboxylic acid, i, 163.
 o-Cymylcarboxylic acid, i, 465.
 m-Cymylglyoxylic acid, i, 163.
 o-Cymylmethylketoxime, i, 464.
 Cytisine, i, 119.

D.

- Dahllite, ii, 421.
 Danalite, ii, 215.
 Dandruff of the horse, ii, 585.
 Decaglycerol, i, 663.
 Decanaphthene acetate, i, 636.
 — alcohol, i, 636.
 — from Caucasian petroleum, i, 635.
 Decane, critical constants of, ii, 446.
 — magnetic rotation of, ii, 442.
 Decylene, magnetic rotation of, ii, 442.
 Dehydracetic acid, amido-, TRANS., 128.
 — formation of, from acetic chloride, i, 92.
 — — formation of orcinol and other condensation products from, TRANS., 122.
 — — production of naphthalene derivatives from, TRANS., 329.
 α -Dehydroamaric acid, i, 590.
 β -Dehydroamaric acid, i, 590.
 Dehydroamaric anhydride, i, 590.
 Dehydrodiacetyllevulinic acid, action of benzaldehyde on the ammoniacal derivatives of, i, 177.
 Dehydrophotosantonin acids, i, 665.
 Dehydropropionylacetic acid, i, 400.
 Densities of certain gases, ii, 453, 514.
 Density and composition of sulphuric acid solutions, ii, 61, 155.
 — maximum, of aqueous solutions, temperature of, ii, 60.
 — of solids, discoverer of the method of determining by suspension, ii, 508.
 Deoxyamalic acid, i, 406.
 — — thermochemistry of, ii, 361.
 Deoxybenzoïn, condensation of benzaldehyde with, i, 353.
 — condensation of, with aldehydes and ketones, i, 589.
 — condensation of, with acetophenone and with furfuraldehyde, i, 526.
 Deoxydigitogenic acid, i, 666.
 Depolarisers, nature of, PROC., 1893, 148, 188.
 Dermatol, i, 643.
 Descloizite from the Obir, ii, 577.
 Desiccators, vacuum, tap for, ii, 453.
 Desmine from Brazil, ii, 423.
 Desmotroposantonin, i, 526.
 Desmotroposantonous acid, i, 527.
 Desylacetophenone, formation of, i, 219.
 Desylanilide, i, 519.
 Desyl- β -naphthalide, i, 520.
 Desylparatoluidide, i, 519.
 Dextrin, molecular mass of, i, 7.
 Dextrins from starch, i, 127.
 Dextroethoxysuccinic acid, TRANS., 234.
 Dextromenthone, amine from, i, 224.
 Dextromethoxysuccinic acid, TRANS., 223.
 Dextrose, i, 191.
 — benzoate, i, 186.
 — birotation and hydrazone-formation of, i, 126.
 — estimation of, ii, 248.
 — formation of, from starch, i, 4.
 — in blood, ii, 81.
 — physiological conversion of maltose into, ii, 23.
 — saccharose, and levulose, analysis of a mixture of, ii, 99.
 Dextroterpenes in Russian turpentine, valency of, i, 358.
 Diabetes mellitus, metabolism in, ii, 177.
 — pancreatic, ii, 31.
 — phloridzin, ii, 31, 480.
 — in frogs, ii, 480.
 Diabetic coma, ii, 543.
 Diabetics, behaviour of galactose in, ii, 177.
 Diacetylhydroxamic acid, PROC., 1893, 77.
 Diacetoxyhexahydrobenzoic acid, i, 35.
 σ -Diacetoxytrithiobenzene, i, 331.
 Diacetyl, preparation of, from tetric acid, i, 690.
 Diacetyl- β -benzylhydroxylamine, i, 707.
 Diacetylcitrazinamide, TRANS., 1038.
 Diacetyldianilidosuccinic anhydride, i, 566.
 Diacetyldi- α -naphthylethylenediamine, i, 99.
 — dibromo-, i, 99.
 Diacetyldi- β -naphthylethylenediamine, i, 100.
 — dibromo-, i, 100.
 Diacetyldiorthotolyethylenediamine, i, 79.
 — dibromo-, i, 79.
 Diacetyldiparatoluidosuccinic acid, i, 566.
 Diacetyldiparatolyethylenediamine, i, 79.
 — dibromo-, i, 79.
 Diacetyldiphenyldihydrotetrazine, i, 711.
 Diacetyldiphenylethylenediamine, dibromo-, i, 78.
 — dichloro-, i, 78.
 Diacetylglyceric acid, ethereal salts of, and their relation to optical activity, TRANS., 1419.
 Diacetylhomocatechol, i, 259.
 2:6-Diacetylheptane, reduction products of, TRANS., 111.
 Diacetylnicotine, i, 675.
 Diacetylorthocyanobenzyl cyanide, i, 228.
 Diacetylpinacone, i, 245.
 Diacetyltartaric acid, ethereal salts of, i, 73.
 Dialkylorthotoluidines, metamido-, i, 409.

- Diallyl, action of mercuric chloride on, i, 450.
 — dihydrido-, stereoisomeric, i, 237.
 — heat developed by the union of bromine with, ii, 444.
 — preparation of, i, 237.
 — stereoisomeric tetrabromides of, i, 237.
 Diallyldiparatolyltetrazone, i, 704.
 Diallyloxalic acid, oxidation of, i, 12.
 Diallyloxanilorthamidoditolyamine, i, 325.
 Dialuric acid, thermochemistry of, ii, 361.
 Diamines, rotatory power of salts of, ii, 105, 106.
 Damines, ortho-, derivatives of, i, 283.
 — — — oxidation products of, i, 266, 324.
 Diamond, artificial production of, ii, 519.
 — existence of, in the meteoric iron of Cañon Diablo, ii, 174, 288.
 — origin of the, ii, 285.
 Diamonds, artificial production of, ii, 276, 277.
 — ash of, ii, 319.
 — ignition temperature of, ii, 319.
 — in blue earth from the Cape, ii, 285.
 — properties of, ii, 319.
 Diamylene, i, 382.
 — critical temperature of, ii, 446.
 Diamylphenylthiocarbamide, i, 575.
 Diamylthiocarbamine chloride, i, 576.
 Dianildiazoxyphenetol, i, 328.
 $\alpha\gamma$ -Dianilidoquinoline, i, 728.
 Dianilidosuccinic acid, i, 565.
 — — — derivatives of, i, 565.
 Dianilsuccin, i, 565.
 Dianisyl dinitrosacyl, action of aniline on, i, 206.
 Dianisyltrichlorethane, i, 272.
 Diapocinchonine, i, 678.
 Diastase, i, 744.
 — from wheat, i, 743.
 — of leaves, *TRANS.*, 604.
 — — — action of, on soluble starch, *TRANS.*, 651.
 — — — periodic variations of the, *TRANS.*, 644.
 — — — products of the transformation of starch by, *TRANS.*, 634.
 — — — occurrence of, in the leaf, *TRANS.*, 633.
 — — — Reychler's artificial, i, 744.
 Diastases, chemical conditions of the actions of, i, 187.
 Diastatic action of the serum of blood and lymph, ii, 333.
 — activity of leaves, determination of, *TRANS.*, 637.
 — ferment in blood, ii, 581.
 Diastatic ferments in the organism, influence of carbonic anhydride on, ii, 475.
 Diazine derivatives, para-, i, 374.
 Diazoacetophenone, i, 570.
 Diazoamidobenzene benzoate, i, 331.
 — — — metanitrobenzoate, i, 331.
 Diazoamidobenzenetetrahydroisoquinoline, i, 528.
 Diazoamido-compounds, i, 201.
 Diazoamidodihydromethylketole, i, 468.
 Diazoamidonitrotoluene, i, 46.
 Diazoamidoparatoluonitrile, preparation of, i, 201.
p-Diazoamidotoluene benzoate, i, 331.
 — — — metanitrobenzoate, i, 331.
 Diazobenzene, action of, on ethylic acetate, i, 84, 156.
 — — — action of, on β -ketonic acids, i, 156.
 — — — action of, on malonic acid, i, 82.
 — — — action of phenylhydrazine on, i, 509.
 — — — behaviour of, towards potassium ferricyanide, i, 326.
 — — — behaviour of, towards potassium permanganate, i, 327.
 — — — chloride, action of benzene or toluene on, i, 701.
 — — — action of diphenyl on, i, 701.
 — — — derivatives of, i, 200.
 — — — perbromide, i, 90.
 — — — sulphate, decomposition of, in amyl alcohol, i, 639.
 — — — — — metanitro-, decomposition of, in amyl alcohol, i, 639.
 Diazobenzenimide, action of, on methylic acetylenedicarboxylate, i, 570.
 — — — bromonitro-, i, 90.
 — — — 1 : 2 : 4-dinitro-, i, 202.
 — — — diorthobromoparanitro-, i, 90.
 — — — metanitro-, i, 91.
 — — — orthonitro-, i, 91.
 — — — orthoparadinitro-, i, 91.
 — — — paranitro-, i, 90.
p-Diazobenzenesulphonic acid, reaction of alcohols with, i, 639.
 Diazo-compounds, action of, on hydrazines, i, 202.
 — — — aromatic, i, 154.
 — — — decomposition of, i, 325.
 — — — decomposition of, by water, i, 81.
 Diazoimides, conversion of amines into, by means of azoimide, i, 202.
 Diazometaxylenimide, metanitro-, i, 92.
 Diazonaphthalene chloride, action of benzene on, i, 701.
 β -Diazonaphthalene, bromo-, i, 705.
 1 : 3'-Diazonaphthalenesulphonic acid, i, 654.
o-Diazophenol chloride, action of sodium sulphide on, i, 330.
 Diazotetrazole, i, 440.

- Diazotetrazotic acid, salts of, i, 441.
 Diazotoluene chlorides, action of benzene or toluene on, i, 701.
p-Diazotoluene, bromo-, i, 705.
o-Diazotolueneimide, metanitro-, i, 91.
 ——— paranitro-, i, 82.
p-Diazotolueneimide, orthonitro-, i, 92.
p-Diazotoluenemetasulphonic acid, action of alcohols on, i, 585.
p-Diazotolueneorthosulphonic acid, action of alcohol on, i, 325.
 ——— action of methyl alcohol on, i, 585.
 Dibenzamide, i, 29.
 Di- γ -benzamidodipropylacetic acid, i, 687.
 Di- γ -benzamidodipropylmalonic acid, i, 687.
 Dibenzeneazodi- β -naphtholmethane, i, 172.
 Dibenzenedisulphonic acid, thio-, i, 416.
 Dibenzenesulphodihydroaldine, i, 213.
 Dibenzenesulphonebenzidine, i, 168.
 Dibenzenesulphonedimethylbenzidine, i, 168.
 Dibenzenyldiazine, i, 711.
 Dibenzimidine, i, 711.
 Dibenzacetophenonetetraureide, i, 649.
 Dibenzoxycarbamide, i, 702.
 Dibenzoylazoxazole, i, 355.
 Dibenzoyl- β -benzylhydroxylamine, i, 706.
 Dibenzoyldiamidoethylene, i, 200.
 α -Dibenzoyldiamidoethylene, i, 437.
 β -Dibenzoyldiamidoethylene, i, 437.
 Dibenzoyldiamidonitrotertiarybutylbenzene, i, 637.
 Dibenzoyldihydroxybenzylpyridine, TRANS., 261.
 Dibenzoyldi- β -naphthylethylenediamine, i, 100.
 Dibenzoylglyoxime, i, 355.
 Dibenzoylorthamidophenylethylamine, i, 609.
o-Dibenzoylphenylenediamine, nitro-, i, 437.
 Dibenzoyltetrahydrophthalazine, i, 733.
 Dibenzyl, amido-, i, 354.
 Dibenzyladonitol, i, 292.
 Dibenzylamine, preparation of, TRANS., 1311.
 ——— thiocyanate, i, 412.
 Dibenzylaminephenylsulphone, i, 203.
 Dibenzylaniline, orthodiamido-, i, 198.
 Dibenzylchloramine, i, 296.
 Dibenzylcyanacetic acid, i, 17.
 1 : 4-Dibenzyl-2 : 5-diphenylpiazine dihydride, TRANS., 1362.
 1 : 4-Dibenzyl-2 : 6-diphenylpiazine dihydride, TRANS., 1366.
 ——— action of ferric chloride on, TRANS., 1373.
 1 : 4-Dibenzyl-2 : 6-diphenylpiazine dihydride, molecular transpositions of, TRANS., 1371.
 3 : 5-Dibenzyl-2 : 6-diphenylpiazine, TRANS., 1371.
 Dibenzylmetadimidobenzene, orthodinitro-, i, 198.
 Dibenzylorthodiamidotoluene, orthodinitro-, i, 198.
 Dibenzylparatoluidine, dinitro-, derivatives of, i, 198.
 ——— orthodiamido-, i, 198.
 Dibenzylphenolphthalein, i, 420.
 Dibenzylthiocarbamic chloride, i, 412.
 Dibenzylthiocarbamide, unsymmetrical, i, 411.
 Dibiphenylethylene, i, 38.
 Dibutyldiphenylethylenediamine, tetranitrotertiary-, i, 700.
 Dibutyramide, γ -thio-, i, 8.
 Dibutyryldi- α -naphthylethylenediamine, di- α -bromo-, i, 99.
 Dibutyryldi- β -naphthylethylenediamine, di- α -bromo-, i, 100.
 Dibutyryldiorthotolylethylenediamine, di- α -bromo-, i, 79.
 Dibutyryldiparatolylethylenediamine, di- α -bromo-, i, 79.
 Dibutyryldiphenylethylenediamine, di- α -bromo-, i, 79.
 Dibutyryltartaric acid, ethereal salts of, i, 73.
 Dicaprylcarbinol, TRANS., 455.
 Dicarboxylic acids, asymmetrical, i, 251.
 Dicarboxyphenylglyoxylic acid, i, 593.
 Dichloralantipyrine, i, 301.
 Dicinchonine, i, 678.
 Dicinnamylamine, i, 569.
 Di- ψ -cumyldichlorethylene, i, 271.
 Di- ψ -cumyldichlorethylenedisulphonic acid, i, 271.
 Di- ψ -cumylethane, asymmetrical, i, 271.
 Di- ψ -cumylketodisulphonic acid, i, 271.
 $\alpha\beta$ -Dicumyl- α' -phenylfurfuran, i, 219.
 Di- ψ -cumyltrichlorethane, i, 271.
o-Dicyanobenzylacetoneitrile, i, 17.
 Dicyanodiamide, constitution of, i, 494.
 ——— detection of, i, 494.
 ——— reduction of, i, 494.
 Diet, proteid in, ii, 540.
 α -Diethoxydinaphthostilbene, i, 272.
 α -Diethoxydinaphthyltrichlorethane, i, 272.
 β -Diethoxydinaphthyltrichlorethane, i, 272.
 Diethyl ketone, magnetic rotation of, ii, 442.
 ——— specific volume and thermal expansion of, TRANS., 285.
 Diethylamide, bromyl-, i, 305.
 ——— dichloryl-, i, 192.

- Diethylamine, depression of the freezing point of benzene by, TRANS., 1021.
 — freezing points of aqueous solutions of, TRANS., 158.
 — hydrates of, TRANS., 160.
p-Diethylbenzene, i, 408.
 Diethyldibenzenesulphoneparaphenylenediamine, dibromo-, i, 168.
 Diethyldiphenoxymethane, i, 214.
 Diethylene oxide sulphone, i, 459.
 Diethylenetriphenylhydrazines, isomeric, i, 571.
 Diethylhydroxyazoxazinedicarboxylic acid, i, 398.
 Diethylic camphorate, action of phenylhydrazine on, i, 600.
 — metahydroxyuvitate, i, 252.
 — 5-phenylpyrazoline-3 : 4-dicarboxylate, i, 282
 — pyrotartrate, i, 251.
 Diethylisopropylcarbinol, i, 124.
 Diethyl- β -methyladipic acid, i, 130.
 Diethylphenylthiocarbamide, i, 576.
 Diethylorthotolidine, metamido-, i, 77.
 — metanitro-, i, 77.
 Diethylparatoluidineorthosulphonic acid, i, 584.
 Diethylphenylthiocarbamide, i, 575.
 Diethyltetrahydronaphthylalkaline, i, 592.
 Diethylthiocarbamine chloride, i, 576.
 Diethyltoluidine hydrochloride, i, 584.
 Diffusibility of certain gases through a caoutchouc membrane, ii, 564.
 Diffusion in aqueous salt solutions, ii, 265.
 — of aqueous solutions of mixed salts, ii, 565.
 — of oxygen and nitrogen in water, ii, 62.
 — of substances in solution, ii, 155.
 — phenomena of solutions, new method of studying, ii, 109.
 — — with precipitate membranes, ii, 203.
 — rate of, of dextro- and lævo-rotatory tartaric acid, ii, 316.
 — theory of, ii, 109.
 $\beta\delta$ -Difurfurallevulinic acid, i, 254.
 Difurfuraltriureide, i, 647.
 $\beta\delta$ -Difurfuryllevulinic acid, i, 255.
 Digestibility of bread, ii, 24, 580.
 — of milk, ii, 580.
 — of proteid, influence of salt on, ii, 579, 580.
 Digestion, artificial, influence of tea and coffee on, ii, 540.
 — influence of increased or diminished consumption of food and of the salts added to the food on, ii, 132.
 — influence of salt on, ii, 579, 580.
 — natural and artificial, ii, 423.
 — peptic, influence of chloroform on, ii, 217.
 Digestive fluids, behaviour of sterilised milk towards, ii, 217.
 Digitogenin, derivatives of, i, 665.
 Digitoic acid, i, 666.
 Digitonin, preparation of pure, i, 665.
 Diglycollaldehyde, i, 617.
 Diglycollanil, i, 191.
 Diglycollanilic acid, thio-, i, 191.
 Diglycollanilide, i, 191.
 — thio-, i, 191.
 Diglycollic acid, i, 191.
 — anhydride, thio-, i, 191.
 — chloride, i, 191.
 Diglycollparatolilic acid, thio-, i, 191.
 Dihydrobenzaldehyde, i, 341.
 Dihydrobenzaldoxime, action of bromine on, i, 332.
 Dihydrobenzamide, i, 341.
 Dihydrobenzene, i, 255.
 Dihydrobenzoic acid, bromine derivatives of, i, 341.
 Dihydrocarveol, i, 359, 595.
 — oxidation of, i, 597.
 Dihydrocarveyl phenylurethane, i, 595.
 Dihydrocarvone, i, 595.
 Dihydrocarvylamine, i, 595.
 Dihydro- ψ -cumene, i, 597.
 Dihydrocymene, synthesis of a, i, 258.
 Dihydrodiethylbenzene, i, 258.
 Dihydrodiphthalylldiimide, i, 372.
 Dihydro-2'-ethylquinazoline, i, 51.
 Dihydro-3'-ethylquinazoline, i, 51.
 Dihydroisocoumarincarboxylic acid, i, 592.
 Dihydroisindole, i, 347.
 Dihydroisquinoline, i, 418, 530.
 Dihydropmethyleketole, i, 468, 520.
 — paramido-, i, 469.
 — paranitroso-, dinitroso-, and nitro-nitroso-, i, 521.
 Dihydronaphthalene and its derivatives, i, 591.
 Dihydronaphthol, i, 592.
 Dihydropiazone, dichloro-, i, 371.
 Dihydrophenonaphthacridine, i, 476.
 Dihydro-2'-phenylquinazoline, i, 50.
 Dihydroxyanthraquinoneformamides, i, 659.
 Dihydroxybenzopinacolin, i, 354.
 Dihydroxybenzoylbenzenesulphonic acid and its salts, i, 94.
 Dihydroxybenzoyltrimethoxymethane, i, 417.
 Dihydroxybenzylpyridine, TRANS., 259.
 Dihydroxycitronellie acid, i, 685.
 Dihydroxydiketotetrahydronaphthalene, azines and euhodoles from, i, 356.
 Dihydroxydimethylglutaric acid dihydrazide, i, 73.
 Dihydroxyhexahydrobenzoic acid, i, 34.
 Dihydroxyhydrindene, imido-, i, 519.

- Dihydroxyhydrolapachol, bromo-,
 TRANS., 428.
 Dihydroxymethylhydrastimide, i, 119.
 Dihydroxynaphthoic acid, i, 356.
 β -Dihydroxynaphthoic acids, i, 475, 476.
 Dihydroquinazolines, formation of,
 i, 438.
 Dihydroxypyridines, i, 527; TRANS.,
 874.
 — action of bromine on, i, 527.
 Dihydroxysantogenenic acid, i, 111.
 Dihydroxytartaric acid, hydrazone of,
 i, 147.
 Dihydroxytetrahydronaphthylethylenedi-
 amine, i, 592.
 Dihydroxythiobenzenes, constitution of,
 i, 461.
 Dihydroxytropidine, i, 738.
 Diisoamylthiourea, TRANS., 322.
 Diisobutylamide, bromyl-, i, 305.
 — chloryl-, i, 192.
 Diisobutylthiourea, symmetrical,
 TRANS., 319.
 Diisobutyryldi- α -naphthylethylenedi-
 amine, di- α -bromo-, i, 99.
 Diisobutyryldiorthotolythylenedi-
 amine, di- α -bromo-, i, 79.
 Diisobutyryldiparatolythylenediamine,
 di- α -bromo-, i, 79.
 Diisobutyryldiphenylethylenediamine,
 di- α -bromo-, i, 79.
 Diisoeugenol, preparation of, i, 643.
 Diisohexolactone, i, 690.
 Diisohexonic acid, i, 690.
 Diisopropylbenzene, constitution of,
 i, 562.
 Diketodinaphthylmethane, i, 172.
 α -Diketohydrindene, hexachlor-, i, 345.
 $\alpha\gamma$ -Diketohydrindenecarboxylic acid,
 sodium salts of, i, 415.
 $\alpha\gamma$ -Diketohydrindone derivatives, con-
 version of phthalide derivatives into,
 i, 415.
 Diketomethylpentachlorhexamethylene
 [1 : 3 : 5], i, 259.
 Diketomethylpentene, dichloro-, i, 260,
 319.
 — trichloro-, i, 319.
 α -Diketones, reduction of, TRANS.,
 770.
 β -Diketones, condensation of, with carb-
 amide and thiocarbamide, i, 129.
 1 : 5-Diketones, synthesis of, i, 419.
 Diketopentene, dichloro-, i, 319.
 — symmetrical and unsymmetrical
 trichloro-, i, 319.
 $\alpha\alpha$ -Diketotetrahydronaphthalene oxide,
 i, 220.
 Dilactide, i, 166.
 Dilactylic acid, trithio-, i, 308.
 Dilatometers, construction of, TRANS.,
 263.
 Dilution, influence of, on the velocity of
 chemical reactions, ii, 510.
 Dimesitylthiocarbamide, i, 32.
 p -Dimethoxybenzophenone, i, 97.
 p -Dimethoxybenzophenoneoxime, i, 97.
 Dimethoxydichloroquinone, methyl and
 ethyl alcoholates of, i, 563.
 2 : 3-Dimethoxyphenyl-1 : 4-dibenzoyl-
 piazine dihydride, TRANS., 1303.
 2 : 3-Dimethoxyphenylpiazine, TRANS.,
 1303.
 — 5 : 6-dihydride, TRANS., 1300.
 2 : 3-Dimethoxyphenylpiazinecarboxyl-
 amide, TRANS., 1308.
 2 : 3-Dimethoxyphenylpiazinecarboxylic
 acid and its salts, TRANS., 1308.
 Dimethoxyphthalazone, i, 371.
 Dimethoxyquinone, symmetrical, i, 409.
 3 : 3'-Dimethyl-2-aceto-1 : 1'-dinaph-
 thol, TRANS., 334.
 Dimethylacetylacetone, i, 454.
 Dimethylacetylbenzimidazole
 [2 : 2' : 3'], i, 434.
 Dimethylacetylpyrrolone [3 : 5 : 3],
 i, 623.
 Dimethylacetylpyrrolines and dimethyl-
 diacetylpyrrolines, salts of, i, 602.
 Dimethylallene, action of mineral acids
 on, i, 541.
 Dimethylamaric acid, i, 590.
 Dimethylamide, bromyl-, i, 305.
 p -Dimethylamidoazobenzene, reduction
 of, i, 330.
 Dimethylamidoquinoline [1 : 2' : 2],
 i, 604.
 Dimethylamidoquinoline [2' : 4' : 4 or
 2' : 4' : 2], i, 605.
 Dimethylamidoquinolinecarboxylic acid
 [1 : 2' - 2 : 4], i, 604.
 Dimethylamidoquinolinesulphonic acid
 [1 : 2' : 2 : 4], i, 604.
 Dimethylamine, freezing points of
 aqueous solutions of, TRANS., 151.
 — hydrates of, TRANS., 150.
 — platinumchloride, dimorphism of,
 i, 387.
 Dimethylaniline, action of acetic an-
 hydride on, i, 23.
 — methylaniline and aniline, estima-
 tion of, i, 23.
 — nitroso-, action of acid chlorides
 on, i, 564.
 — — action of benzoic chloride on,
 i, 564.
 — paramido-, formyl derivative of,
 i, 509.
 — solutions, action of light on,
 ii, 484.
 — thio-, i, 525.
 Dimethylaticonic acid, i, 692.
 2 : 2'-Dimethylbenzimidazole, chloro-,
 i, 434.

- 2 : 2'-Dimethylbenzimidazole, trichloro-, i, 434.
 2 : 2 -Dimethylbenzimidazole-chloral, i, 438.
 Dimethylbenzylbenzimidazole [2 : 2' : 3'], i, 433.
 Dimethyl- α -bis-diphenylformamidyl-phenylhydrazine, i, 463.
 Dimethylchloramine, i, 497.
 Dimethylchlorobenzimidazole [2 : 2' : 3'], i, 434.
 ——— chloro-derivatives of, i, 434, 435.
 Dimethylcoumalinic acid, bromo-, i, 403.
 Dimethylcyanisocarbostyryl [2' : 3' : 4'], i, 228.
 3 : 7-Dimethyl-2 : 8-diacetoxynonane, TRANS., 120.
 Dimethyldiacetylene, i, 239.
 ——— tetrabromide, i, 239.
 Dimethyldiacetylfurfuran [2 : 5 : 2 : 3], i, 631.
 Dimethyldiethylethylene, asymmetrical, i, 125.
 Dimethyldiethylphenyldithiobiuret, i, 576.
p-Dimethyldihydrobenzylaminecarboxylic acid, i, 378.
n-Dimethyldihydromethylketolium hydroxide, i, 521.
 3 : 7-Dimethyl-2 : 8-dihydroxynonane, TRANS., 119.
 Dimethyldiphenoxymethane, i, 214.
 $\beta\beta$ -Dimethyl- $\gamma\gamma$ -dipiperidyl, i, 613.
 Dimethyldipropylphenyldithiobiuret, i, 576.
 $\beta\beta$ -Dimethyldipyridyl, i, 612.
 Dimethylethylcarbinol, specific volume and thermal expansion of, TRANS., 280.
 Dimethylethyldiphenyldithiobiuret, i, 576.
 α -Dimethylethyldiphenylpseudodithiobiuret, i, 576.
 β -Dimethylethyldiphenylpseudodithiobiuret, i, 577.
 Dimethylethylenediphenylcarbamide, i, 81.
 Dimethylethylmethane, specific volume and thermal expansion of, TRANS., 275.
 Dimethylethylpiperazine [2 : 5 : 3], i, 488.
 Dimethylethylpyrazine [2 : 5 : 3], i, 486.
 Dimethylethylthiocarbamide, i, 576.
 $\alpha\beta$ -Dimethylfurfuran- β -carboxylic acid, i, 403.
 Dimethylglutaric acid, dibromo-, i, 72.
 ——— acids, bromination of, i, 72.
 ——— stereoisomeric derivatives of, i, 72.
 Dimethylglutaric anhydride, dibromo-, i, 73.
 2-Dimethylhydrindole, synthesis of, i, 37.
 Dimethylhydroxytetrahydronaphthylpropionic acid, i, 527.
 Dimethylhypoxanthine, i, 736.
 Dimethylic phenylpyrazolinedicarboxylate, i, 282.
 ——— pyrotartrate, i, 251, 307.
 ——— tetramethylenedicarboxylate, i, 693.
 2' : 3'-Dimethylisocarbostyryl, i, 228.
*B*₁-Dimethylisorosinduline, i, 336.
 Dimethylketohexamethylene, formation of, from dimethylpimelic acid, PROC., 1893, 68.
 Dimethylketohexaphane [2 : 6 : 1], formation of, from dimethylpimelic acid, PROC., 1893, 68.
 Dimethyllevulinic acid, preparation of, i, 72.
 Dimethylmaleic anhydride, action of chlorine on, i, 142.
 $\alpha\beta$ -Dimethylmalic acid, i, 146.
 Dimethylmandelic acid, i, 160.
 Dimethylorthotoluidine bisulphide, amido-, i, 76.
 ——— mercaptan, amido-, i, 76.
 ——— metamido-, i, 76.
 ——— metanitro-, i, 76.
 Dimethylparabanic acid, thermochemistry of, ii, 360.
 Dimethylparatoluylenediamine hydrogen thiosulphate, i, 76.
 Dimethylphenanthroline, i, 605.
 2' : 4'-Dimethylphenometadiazine, i, 530, 531.
 Dimethylphenylthiocarbamide, i, 575.
 Dimethylphenylthiosemicarbazide, i, 29.
 Dimethylphenyltrimethylenediamine, i, 673.
 ——— trimethyltrimethyleneanilthiocarbamate, i, 673.
 Dimethylphthalide, action of alkalis on, i, 644.
 Dimethylphthalidecarboxylic acid, i, 665.
 Dimethylpimelic acid, formation of the ketone 2 : 6-dimethyl-1-ketohexaphane from, PROC., 1893, 68.
 2 : 5-Dimethylpiperazine, i, 487.
 β -Dimethylpiperazine, i, 488.
 Dimethylpiperazylhydrazine, i, 488.
 Dimethyl- α -propionylthetine, i, 633.
 Dimethyl- β -propionylthetine, i, 633.
 Dimethylpropylmethane, specific volume and thermal expansion of, TRANS., 276.
 Dimethylpyrazine, i, 734.
 2 : 5-Dimethylpyrazine, i, 486.

- Dimethylpyrazinecarboxylic acid
 [2 : 5 : 3], i, 487.
 3 : 5-Dimethylpyrazole, i, 178.
 3 : 4-Dimethylpyrazole picrate,
 i, 673.
 Dimethylpyrimidine, amido-, i, 454.
 Dimethylquinol, chlorination of, i, 21.
 Dimethylresorcinol, i, 21.
 — condensation of, with nitrobenz-
 aldehydes, i, 216.
 Dimethylsuccinic acids, sp. gr. of, i, 11.
 Dimethyltetrahydronaphthylalkine,
 i, 592.
 Dimethyltetrahydroquinoline,
 i, 227, 603.
 Dimethylthiocarbamine chloride, i, 576.
 4 : 5-Dimethylxanthone, i, 217.
 Dimyristylcarbinol, TRANS., 459.
 Dimyristylcarbiny acetate, TRANS.,
 459.
 Dinaphthalidonaphthaquinoneanilide,
 i, 339.
 Di- α -naphtholethane, trichloro-, i, 173.
 Di- α -naphtholmethane, i, 173.
 Di- β -naphtholmethane, i, 172.
 Dinaphthosalicylresorcinol, i, 218.
 α -Dinaphthostilbene, i, 272.
 Dinaphthoxanthen, i, 222.
 Dinaphthylamidophosphoric acid,
 i, 324.
 Di- β -naphthylearbamide, i, 99.
 α -Dinaphthyl- $\alpha\gamma$ -diketo- $\beta\delta$ -dimethyl-
 piperazine, i, 52.
 β -Dinaphthyl- $\alpha\gamma$ -diketo- $\beta\delta$ -dimethyl-
 piperazine, i, 52.
 Di- α -naphthyl- $\alpha\beta$ -diketopiperazine,
 i, 55.
 Di- β -naphthyl- $\alpha\beta$ -diketopiperazine,
 i, 55.
 α -Dinaphthyldimethylmethane oxide,
 i, 216.
 α -Dinaphthylethane, asymmetrical,
 i, 272.
 — dibromo-, i, 272.
 Di- α -naphthylethylenediamine hydro-
 bromide, i, 99.
 Di- α -naphthylformazyl methyl ketone,
 i, 159.
 α -Dinaphthylie oxide, dibromo-, i, 275.
 β -Dinaphthylie oxide, bromo-, chloro-,
 and nitro-derivatives of, i, 274.
 β -Dinaphthylketopiperazine, i, 53.
 Di- β -naphthylmetaphenylenediamine,
 i, 421.
 α -Dinaphthyloxidetrichlorethane, i, 272.
 β -Dinaphthyloxidetrichlorethane, i, 272.
 Di- α -naphthylpropylenediamine, i, 81.
 Dinitrosaclys, action of amines and am-
 monia on, i, 205.
 Dinonylcarbinol, TRANS., 457.
 Diopianhydrazonic anhydride, i, 371.
 Diopsides, ii, 130.
 Dioprase from the Congo, ii, 421.
 Dioxindole, thermochemistry of,
 i, 649.
 Dioxyarspariteine, derivatives of, i, 232.
 Dipentene dihydrochloride, hydrocarb-
 ons derived from, TRANS., 292.
 — oxidation of, TRANS., 294.
 Diphenacylbenzylamine, TRANS., 1365.
 — amido-, TRANS., 1365.
 — preparation of, TRANS., 1359.
 — salts of, TRANS., 1364.
 Diphenic acid, β -diamido-, i, 280.
 Diphenoxydichloroquinol, i, 322.
 Diphenoxydichloroquinone, i, 322.
 Diphenyl, magnesium compound of,
 PROC., 1893, 80.
 — orthodiamido-, i, 96, 588.
 — — — action of, on benzile
 i, 96.
 2 : 3-Diphenyl 1 : 4-dihydride, TRANS.,
 1293.
 Diphenylacetamide, i, 590.
 Diphenylacetanilide, i, 590.
 Diphenylacetic acid, i, 390, 590.
 — hydrazine, i, 590.
 Diphenylacetoneitrile, i, 590.
 Diphenylacetylpyrazole [1 : 5 : 3],
 i, 610.
 Diphenylallylthiosemicarbazide, i, 29.
 Diphenylamidokyanidine, i, 735.
 Diphenylamine, orthamido-, action of
 ferric chloride on, i, 199.
 Diphenylanilguanidine and its deriva-
 tives, i, 25.
 Diphenylanilidokyanidine, i, 735.
 Diphenylauramine, i, 473.
 Diphenyldiacetylene tetriodide, i, 2.
 2 : 3-Diphenyl-1 : 4-diacetylpiazine di-
 hydride, TRANS., 1296.
 2 : 3-Diphenyl-1 : 4-dibenzylpiazine di-
 hydride, TRANS., 1294.
 Diphenyldihydronaphthaquinoxaline,
 i, 284.
 Diphenyldihydrotetrazine, i, 711.
 Diphenyldihydrotoluquinoxaline, i, 284.
 Diphenyldimethylethylenediamine,
 i, 81.
 Diphenyl- α -dimethyl- β -ketopiperazine,
 i, 54.
 Diphenyldimethylpiperazine, i, 80.
 Diphenyldinitrosacyl, i, 205.
 — action of aniline on, i, 205.
 — action of paratoluidine on, i, 206.
 Diphenylcamphoramide, i, 361.
 Diphenylchlorokyanidine, i, 735.
 Diphenyleneimidoketone, i, 417.
 Diphenylenephenylmethane oxide,
 i, 220.
 Diphenylethylenediamine, acidoxyl de-
 rivatives of, i, 78.
 — diorthonitro-, i, 700.
 — diparanitro-, i, 700.

- Diphenylethylenediamine, hexanitro-, i, 700.
 — tetranitro-, i, 700.
 Diphenyl- α -ethyl- β -ketopiperazine, i, 53.
 $\alpha\beta$ -Diphenyl- μ -ethyloxazole, TRANS., 473.
 Di- α -phenylethylthiocarbamide, i, 703.
 Diphenylformazyl methyl ketone, α -para-nitro-, i, 159.
 $\alpha\beta'$ -Diphenylfurfuran, i, 512.
 Diphenylhydrazones, stereochemical, i, 208.
 Diphenylhydroxytriketone, oximes of, i, 169.
 Diphenylic amidophosphate, i, 315.
 Diphenylimidobiazolone, i, 28.
 Diphenylimidobiazolonyl- μ -mercaptide, i, 28.
 Diphenylimidobiazolonyl- μ -methyl sulphide, i, 28.
 2': 3'-Diphenylindoles, i, 519.
 Diphenyl- α -keto- β -methylpiperazine, i, 53.
 $\alpha\beta$ -Diphenyl- μ -methyloxazole, TRANS., 472.
 Di- p -phenylmethyloxybiazoloncarbamide, i, 534.
 Di- p -phenylmethyloxybiazolonethiocarbamide, i, 534.
 2: 3-Diphenyl-3-methylpiazine, TRANS., 1285.
 — picrate, TRANS., 1286.
 Diphenylmethylpyrazoline [1:5:3], oxidation of, i, 229.
 Diphenylmethylpyrazolone [1:5:2:3], i, 230.
 Diphenylmethylthiosemicarbazide, i, 29.
 2: 3-Diphenyl- β -naphthindole, i, 520.
 2': 3'-Diphenylorthotolindole, i, 520.
 Diphenylsotriazolidinecarboxylic acid, i, 565.
 $\alpha\beta$ -Diphenyloxazole, TRANS., 470.
 2': 3'-Diphenylparatolindole, i, 520.
 Diphenylphenylhydrazokyanidine, i, 735.
 Diphenylphthalide, action of phenylhydrazine on, i, 473.
 2: 4-Diphenylpiazine, TRANS., 1297.
 2: 5-Diphenylpiazine, TRANS., 1363.
 2: 6-Diphenylpiazine, TRANS., 1368.
 2: 3-Diphenylpiazinecarboxylamide, TRANS., 1304.
 2: 3-Diphenylpiazinecarboxylic acid and its salts, TRANS., 1305.
 Diphenylpropylenediamine, i, 79.
 Diphenylpyrazole, new synthesis of, i, 44.
 1: 3-Diphenylpyrazole, i, 230.
 1: 5-Diphenylpyrazole, i, 230.
 3: 5-Diphenylpyrazole, i, 231.
 Diphenylpyrazoledicarboxylic acid [1:3:4:5], i, 231.
 Diphenylpyrazoles, isomerism of, i, 230.
 Diphenylpyrazolidinosemicarbazide, i, 611.
 Diphenylpyrazolidinethiosemicarbazide, i, 611.
 Diphenylpyrazolone from cinnamic hydrazide, i, 230.
 β -Diphenylsemithiocarbazide, i, 206.
 Diphenylsulphoneacetone, symmetrical, synthesis of, i, 167.
 Diphenylsulphonemethane, i, 141.
 Diphenylsulphoneortho-xylylenediamine, i, 733.
 Diphenylsulphonethylic oxide, i, 415.
 Diphenyltetraketone, action of phenylhydrazine on, i, 170.
 Diphenyltetraketonedioxime, i, 170.
 Diphenyltetraketoxime, i, 355.
 Diphenyltetrazine, i, 711.
 α -Diphenylthiosemicarbazide, i, 27.
 β -Diphenylthiosemicarbazide, i, 27.
 Diphenylthiosemicarbazides, action of methylic iodide on, i, 27.
 Diphenyltrichlorethane, derivatives of, and their conversion into stilbene, i, 271.
 Diphenylurazine, an isomeric, i, 24.
 Dipthalaldehydehydrazonic acid, i, 372.
 ω -Dipthalimidomesitylene, i, 33.
 Dipropargyl, i, 239.
 Dipropenyl tetrabromides, stereoisomeric, i, 238.
 Dipropenyls, stereoisomeric, i, 238.
 Dipropionitrile, oximido-, i, 315.
 Dipropionyldi- α -naphthylethylenediamine, di- α -bromo-, i, 99.
 Dipropionyldi- β -naphthylethylenediamine, di- α -bromo-, i, 100.
 Dipropionyldiorthotolylethylenediamine, dibromo-, i, 79.
 Dipropionyldiparatolythylenediamine, di- α -bromo-, i, 79.
 Dipropionyldiphenylethylenediamine, dibromo-, i, 78.
 Dipropionyltartaric acid, ethereal salts of, i, 73.
 Dipropylacetic acid, di- γ -amido-, i, 687.
 Dipropylamide, bromyl-, i, 305.
 — chloryl-, i, 192.
 Dipropylamidoacetic acid, i, 554.
 Dipropylamine, freezing points of aqueous solutions of, TRANS., 171.
 — hydrate of, TRANS., 171.
 Dipropylcarbamide, i, 253.
 Dipropylcarbodiimide, i, 297.
 Dipropylchloramine, i, 296.
 Dipropyleyanamide, i, 297.
 Dipropyldiphenoxymethane, i, 214.
 Dipropylethylthiocarbamide, i, 576.
 Dipropylphenylthiocarbamide, i, 575.
 Dipropylthiocarbamide, i, 253.

- Dipropylthiocarbamine chloride, i, 576.
 Dipseudocumylethane, symmetrical bromo-, i, 271.
 Dipyrazolone ketone, i, 428.
 3-Dipyrazolone ketone, i, 730.
 3-Dipyrazolonemethylenephénylhydrazine, i, 730.
 Dipyrityl- $\beta\beta$ -dicarboxylic acid, i, 613.
 Diresorcinol, i, 352.
 Diresorcinoldisulphonic acid, i, 353.
 Diresorcinolsulphone, i, 352.
 Diricinoleinsulphuric acid, i, 455.
 Diricinosulphuric acid, i, 455.
 Disalicylquinol, i, 218.
 Disalicylresorcinol, i, 218.
 Dispersion of isomerides, ii, 1.
 — molecular, ii, 254.
 Dispersions of sulphuric acid solutions, TRANS., 99.
 Dissociation and electrolytic conductivity, ii, 59.
 — electrolytic and ionisation, ii, 4.
 — of acid salts, ii, 365.
 — of salts, determination of, ii, 364.
 — of water, ii, 364, 365, 448.
 — heat of, of some acids, ii, 259.
 — in solutions, ii, 265.
 — measurements of feebly dissociated acids, ii, 62.
 — non-electrolytic, in solutions, ii, 509.
 — of barium peroxide, ii, 71.
 — of calcium plumbate, ii, 524.
 — of chrome alum, ii, 73.
 — of double salts in solution, ii, 110.
 — of saline hydrates and analogous compounds, ii, 364.
 — of salts into their ions by water of crystallisation, ii, 265.
 — of sodium chloride in presence of heated surfaces of porous clay, ii, 315.
 — ratio of salts, ii, 565.
 Dissociation-theory of solution, ii, 565.
 Distillation apparatus for analysis, ii, 487.
 — fractional, ii, 204.
 — under reduced pressure, apparatus for, ii, 267.
 — with superheated steam, laboratory apparatus for, ii, 163.
p-Ditolilsuccin, i, 565.
o-Ditoluidophosphoric acid, i, 323.
p-Ditoluidophosphoric acid, i, 324.
p-Ditoluidosuccinic acid, i, 565.
p-Ditoluyldihydroxytriketone, i, 170.
p-Ditoluyltetraketone hydrate, i, 170.
 Ditolylamine, orthamido-, action of, on alloxan, i, 324.
p-Ditolylamine, orthamido-, i, 283.
 Ditolylecamphoramide, i, 362.
o-Ditolyl- $\alpha\gamma$ -diketo- $\beta\delta$ -dimethylpiperazines, isomeric, i, 52.
p-Ditolyl- α -dimethyl- β -ketopiperazine, i, 54.
 Ditolyleneazone, i, 733.
 Ditolylethylenediamine, acidoxyl derivatives of, i, 78.
p-Ditolyl- α -ethyl- β -ketopiperazine, i, 54.
p-Ditolylformazyl methyl ketone, i, 159.
p-Ditolyl- α -keto- β -methylpiperazine, i, 53.
o-Ditolylketopiperazine, i, 54.
p-Ditolylmethylpiperazine, i, 81.
 Ditolylparaphenylenediamine, tetranitro, i, 15.
p-Ditolylparatolylene-diamine, TRANS., 1408.
o-Ditolylpropylenediamine, i, 80.
p-Ditolylpropylenediamine, i, 81.
 Ditolylsulphonethylic oxide, i, 416.
o-Ditolyl- $\alpha\gamma$ -tetraketoparadiazine, i, 374.
p-Ditolyltriamidotoluene, TRANS., 1402.
 Divinyl glycol and its derivatives, i, 240.
 Dextrin, i, 684.
 Dextrose, fermentation of, by a lævo-lactic ferment, TRANS., 1265.
 — See Glucose, ii, 555.
 Dixanthone, ortho-, i, 218.
 Dixylyldihydroxytriketone, i, 170.
 Dixylyltetraketone, i, 170.
 Dog, influence of dividing the daily nutriment on the metabolism of the, ii, 383.
 Drainage water from arable soils, ii, 338.
 Dropsical fluids, proteids in, ii, 334.
Drosera Whittakeri, colouring matters of, TRANS., 1083.
 Drying oven, ii, 162.
 Dulcitol from Mozambique cane sugar, i, 64.
 Dyeing properties of chay root, TRANS., 1183.
 Dyes, coal tar, qualitative analysis of, ii, 610.
 — substantive cotton, from diamidophenanthraquinone, i, 422.
 Dyke, basic, thought to contain leucite, ii, 539.
 Dynamite, analysis of, ii, 196.
 Dyspepsia, nervous, secretion of hydrochloric acid in, ii, 219.

E.

Earths, approximate determination of the equivalents of, by titration, ii, 465.

- Earths, rare, action of charcoal on solutions of the salts of, ii, 374.
 — anhydrous chlorides of the metals of, ii, 466.
 — fractionation of, ii, 374, 375, 376.
 — fractionation of, by electrolysis, ii, 284.
 Ecgonine and cocaine, separation of, ii, 609.
 — constitution of, i, 378.
nor-r-Ecgonine, i, 537.
l-Ecgonineamide and its derivatives, i, 445.
r-Ecgonineamide and its derivatives, i, 445.
l-Ecgoninenitrile, i, 445.
 Echinochrome, i, 59.
 Eczema, ptomaine from the urine in cases of, i, 614.
 Egg white, proteids of, i, 379.
 Elaidic acid, constitution of, i, 551.
 — hydrazide of, i, 231.
 — transformation of, into oleic and iso-oleic acids, i, 550.
 Elaidin reaction, ii, 559.
 Elasticity of gases, ii, 9.
Elaeagnus angustifolius, physiological meaning of the root nodules of, ii, 33.
 Electric arc, fusion and volatilisation of metals and oxides in the, ii, 507.
 — current, changes at the boundary between solutions of different concentration during the passage of the, ii, 404.
 — discharge, separation and striation of rarefied gases under the influence of, ii, 253.
 Electrical calamine from Wythe Co., Virginia, ii, 286.
 — conductivities of phosphoric acid and its salts, ii, 357.
 — conductivity and freezing point of aqueous solutions of fluorine compounds, ii, 315.
 — of aqueous solutions of organic acids, influence of boric acid on, ii, 506.
 — of flames and gases, ii, 563.
 — of mixtures of weak acids and bases, ii, 356.
 — of solid colloidal silver, ii, 314.
 — energy, conversion of, into chemical energy, ii, 107.
 — furnace, ii, 314, 507.
 Electricity, frictional, influence of, on the formation of amalgams, ii, 441.
 — influence of, on the carburisation of iron by cementation, ii, 527.
 Electrochemical effects on magnetising iron, ii, 404.
 — investigations, ii, 255.
 Electrolysis of alkali salts, ii, 441.
 — of aqueous sulphuric acid, production of hydrogen peroxide in, ii, 108.
 — of metallic formates, ii, 191.
 — of silver nitrate in a vacuum, ii, 4.
 — of sodic ethylic camphorate, *Proc.*, 1893, 43.
 — of steam, ii, 515.
 — of substituted organic acids, i, 640.
 — quantitative analysis by, ii, 305, 391, 495.
 Electrolytes, behaviour of, in mixed solvents, ii, 157.
 — conductivity of, in various solvents, ii, 151.
 — diffusion of dilute solutions of, ii, 155.
 — mixed, chemical equilibrium in, ii, 150.
 — separation of precipitates at the boundary of, ii, 404.
 — thermoelectric phenomena between, ii, 202.
 Electrolytic analysis, electromotive force in, ii, 506.
 — conductivity and dissociation, ii, 59.
 — of stereoisomeric acids, ii, 152.
 — dissociation and ionisation, ii, 4.
 — of acid salts, ii, 365.
 — of salts, determination of, ii, 364.
 — of water, ii, 364, 365, 448.
 Electrometric analysis, ii, 387.
 — study of potassium hydrogen triplatohexanitrite, ii, 256.
 Electromotive force in electrolytic analysis, ii, 506.
 — of galvanic combinations, ii, 150.
 — of oxidation cells, ii, 58.
 — the Clark cell as a standard of, ii, 107.
 — Volta, relation of, to pressure, ii, 256.
 — forces of gold and platinum cells, ii, 149.
 — of mercury, abnormal, ii, 356.
 Electrosyntheses, organic, i, 630.
 Elements and compounds, cohesion of, ii, 155.
 — atomic refractions of the, ii, 253.
 — chemical, the measurement of the relative masses of the atoms of the, *TRANS.*, 1.
 — lectures on inorganic chemistry based on the natural system of, ii, 408.
 — new diagram and periodic table of, *TRANS.*, 852.

- Elements, physical character of the lines of the spark spectra of, ii, 2.
- Elemi resin, terpenes from, i, 100.
- Elimination of carbonic oxide, ii, 288.
- Emetine, estimation of, in ipecacuanha, ii, 397, 560, 608.
- Energy, loss of, due to chemical union, method of measuring, ii, 63.
- Epichlorhydrin, action of sodium on, i, 383.
- β -Epichlorhydrin, i, 4.
- Epilobium alpinum*, analysis of, ii, 593.
- Episarkine, i, 536, 542.
- Equilibria, cyclical, ii, 367.
- Equilibrium, chemical, conditions of, ii, 450, 566.
- — in mixed electrolytes, ii, 150.
- in salt solutions, labile conditions of, ii, 447.
- Equisetum fluviatile*, analysis of, ii, 593.
- *palustre*, analysis of, ii, 593.
- Equivalents, determination of, by conversion of oxides into sulphates, ii, 283.
- of the earths, determination of, by titration, ii, 465.
- Erbia, ii, 376.
- Erucic acid, action of sodium hydrogen sulphite and of sulphurous acid on, i, 549.
- — constitution of, i, 551.
- — oxidation and derivatives of, i, 551.
- Erysipelas, ptomaines from the urine in, i, 183.
- Erysipeline, i, 183.
- Erythritol, specific heat of, ii, 258.
- synthesis of, i, 450.
- Erythroextrin, i, 127.
- Erythrophene, *Proc.*, 1892, 192.
- Eserine, green colouring-matter derived from, i, 741.
- new reaction of, i, 741.
- Essential oils. See Oils.
- Ethanalamine, i, 187.
- Ethane and oxygen, temperature of ignition of a mixture of, ii, 258.
- heat of combustion of, ii, 444.
- nitro-, molecular weight in the liquid state, *Trans.*, 1104.
- Ethenylamidonaphthol, i, 171.
- Ethenylamidoximebenzenesulphone, i, 332.
- Ethnyldiparatolytri amidotoluene, *Trans.*, 1405.
- Ethnylethyltolylenediamine, i, 286.
- Ethnylpara-*n*-methyltolylenediamine, i, 285.
- Ether and water, vapour tension of mixtures of, ii, 264.
- Ethereal hydrogen sulphates, excretion of, in cholera, ii, 290.
- oils. See Oils.
- salts, behaviour of, at high temperatures, i, 512.
- — heats of combustion of, ii, 59.
- — hydrolysis of, by means of aluminium chloride, i, 152.
- silicates, catalytic action of aluminium chloride on, i, 62.
- sulphinates, i, 343, 344.
- Etherification, influence of the constitution of the alcohols on the velocity of, ii, 158.
- velocity of, ii, 9, 158.
- Ethers, decomposition of, by haloïd acids, i, 620.
- simple and mixed, boiling points of, *Proc.*, 1893, 145.
- Ethoxalydiacetoneitrile, i, 397.
- Ethoxyacetanaphthol, pentabromo-, i, 653.
- 3-Ethoxy-4-amidoquinoline, i, 607.
- Ethoxybenzene, action of cinnamic chloride on, i, 163.
- Ethoxy-4-benzoylamidoquinoline, i, 606.
- 3-Ethoxy-4-bromoquinoline, i, 607.
- α -Ethoxybutyro- α -naphthalide, i, 52.
- α -Ethoxybutyro- β -naphthalido- α -butyro- β -naphthalide, i, 52.
- p*-Ethoxydiphenylamine, i, 329.
- α -Ethoxyisobutyro- α -naphthalide, i, 53.
- α -Ethoxyisobutyro- β -naphthalide, i, 53.
- α -Ethoxyisobutyro- β -naphthalido- α -isobutyro- β -naphthalide, i, 53.
- p*-Ethoxymetasulphonaminebenzoic acid, i, 585.
- Ethoxynaphthalene, 1 : 4-amido-, derivatives of, i, 39.
- amidoazo-, i, 40.
- 1 : 4-nitro-, i, 39.
- 3-Ethoxy-4-nitroquinoline, i, 607.
- p*-Ethoxyorthotoluenesulphonic acid, and its derivatives, i, 343.
- Ethoxyorthotoluenitrile, i, 16.
- p*-Ethoxyparamidodiphenylamine and its derivatives, i, 329.
- p*-Ethoxyparanitrosodiphenylamine, i, 329.
- m*-Ethoxyphenyl bisulphide, i, 36.
- α -Ethoxy- γ -phenylamidoquinoline, i, 728.
- Ethoxysuccinic acid, optically active, *Trans.*, 229.
- γ -Ethoxy- Δ^1 -tetrahydrobenzoic acid, i, 34.
- p*-Ethoxytoluenemetasulphonamide, i, 585.
- Ethyl methyl ketone, pinacone from, i, 390.
- Ethylacrylamide, i, 695.
- Ethylamethylcamphonitroketone, i, 109.

- Ethylamide, dichloryl-, i, 192.
 Ethylamine, freezing points of aqueous solutions of, TRANS., 154.
 — hydrates of, TRANS., 156.
 — seleno- and thio-derivatives of, i, 30.
 — sulphite, i, 505.
 Ethylbenzalmereaptal hydrochloride, amido-, i, 31.
 Ethylbenzene, critical constants of, ii, 446.
 — *α*-dibromo-, action of aluminium chloride on, i, 562.
 — magnetic rotation of, ii, 442.
 Ethylbenzenes, chlor-, action of aluminium chloride on, i, 561.
 Ethylbenzhydroximeacetic acid, 501.
 Ethylbenzoic acid, amido-, i, 529.
 Ethylbenzoylactic acid oxime, i, 583.
 Ethylbutylcarbinol from mannitol, i, 246.
 Ethylbutylthiourea, secondary, TRANS., 322.
 Ethylcarbamide, thermochemistry of, ii, 359.
 Ethylcarpaine, i, 740.
 Ethylcitraconic acid, i, 195.
 Ethylcytisine, i, 120.
 Ethyldihydroxypyridine, TRANS., 882.
 — oxidation of, TRANS., 883.
 1-Ethyl-3:5-dimethylpyrazole, i, 674.
 — dichloroplato-, i, 674.
 Ethyldiphenylacetic acid, i, 590.
 Ethyldiphenylacetoneitrile, i, 590.
n-Ethyldiphenyldihydrotoluquin-oxaline, i, 286.
 Ethylene, action of mercuric chloride on, i, 450.
 — action of nitrosyl chloride on, TRANS., 479.
 — and oxygen, ignition point of a mixture of, ii, 258.
 — chlorhydrin, action of phenylhydrazine on, i, 639.
 — heat of combustion of, ii, 444.
 — liquid, refractive index of, ii, 201,
 — tetriodo- preparation of, i, 449.
 Ethylenebenzazimide, i, 574.
 Ethylenediamine, action of nitrophenols on, i, 699.
 — and derivatives of acetoacetic acid, condensation products from, TRANS., 1310.
 — rotatory power of tartrates of, ii, 105.
 Ethylenedibromothymol, i, 316.
 Ethylenediethyldisulphone, i, 460.
 Ethylenediethylsulphone, ii, 289.
 Ethylenedisulphonic acid, i, 460.
 Ethylenesulphonic acid, i, 460.
 Ethylenic bromide, action of phenylhydrazine on, i, 98.
 — chloride, heat of vaporisation of, ii, 446.
 — magnetic rotation of, ii, 442.
 Ethylenic chloride, m. p. of, ii, 357.
 — hydrocarbons, condensation of, with hydrocarbons of the benzene series, i, 635.
 — — hydration of, i, 61.
 — oxide, magnetic rotation and refractive power of, TRANS., 488.
 Ethylethoxyazoxazine, i, 398.
 Ethylethoxyazoxazincarboxylic acid, i, 398.
 Ethylfisetol, action of hydroxylamine hydrochloride on, i, 413.
 Ethylformomereaptal, amido-, i, 31.
 Ethylglyoxalinedicarboxylic acid, i, 281.
 Ethylhomapocinchene, oxidation of, i, 377.
 Ethylhomapocinchenic acid, i, 377.
 Ethylic acetate, heat of vaporisation of, ii, 446.
 — — molecular weight of, in the liquid state, TRANS., 1100.
 — — vapour pressure, molecular volume, and critical constants of, TRANS., 1216.
 — — acetoacetate, action of benzoic chloride on metallic derivatives of, i, 628.
 — — action of diazobenzene on, i, 84, 156.
 — — action of hydrogen bromide on, i, 67.
 — — action of methylenic iodide on, i, 393.
 — — action of phenylhydrazine hydrochloride on, i, 67.
 — — aldureides of, i, 645.
 — — and ethyl salicylate, i, 67.
 — — benzaldehyde and carbamide, interaction of, i, 649.
 — — condensation products of the hydrazide of, i, 367.
 — — constitution of, i, 71.
 — — molecular weight of, in the liquid state, TRANS., 1100.
 — — synthesis of phenols from, i, 697.
 — — acetocyanacetate, condensation of, with phenol, i, 456.
 — — condensation of, with resorcinol, i, 456.
 — — acetomalonate, i, 69.
 — — acetomethylmalonate, i, 69.
 — — acetonedicarboxylate, action of nitrous acid on, i, 397.
 — — acetosodacetate, action of, on ethylic α -bromopropionate, α -bromobutyrate, and α -bromisobutyrate, i, 500.
 — — acetoxyfumarate, i, 629.
 — — β -acetoxyisocrotonate, i, 629.
 — — aceturamidocrotonate, i, 647.
 — — acetylenedicarboxylate, i, 145.

- Ethyllic acetylenedicarboxylate, addition of bromine to, i, 645.
- acetylenediamidocrotonate, i, 648.
- acetylenethylmalonate, i, 69.
- α -acetyl- β' -hydroxyfumarate, i, 629.
- acetylsalicylate, i, 66.
- alcohol, as a solvent, i, 244.
- — depression of the freezing point of acetic acid by, TRANS., 1023.
- — depression of the freezing point of benzene by, TRANS., 1019.
- — depression of the freezing point of water by, TRANS., 1015.
- — heat of vaporisation of, ii, 446.
- — higher alcohols and other impurities in, ii, 393.
- — magnetic rotation of, ii, 442.
- — molecular weight of, in the liquid state, TRANS., 1102.
- — presence of, in oil of roses, ii, 181.
- allylmethylindolecarboxylate, i, 704.
- ammonium mesitencarbamate, hydrate of, i, 554.
- azobenzeneacyanacetate and its derivatives, i, 210, 509.
- 4-azobenzene-pyrazolone-3 carb-oxylate, i, 367.
- azoparotolueneacyanacetate, i, 510.
- azorthotolueneacyanacetate, i, 509.
- benzalpyrazolonecarboxylate, i, 367.
- benzeneazocyanacetate, α - and β -, i, 465.
- benzenesulphinate, action of hydrogen sulphide on, i, 344.
- — preparation of, i, 270.
- benzodiamidodimaleate, i, 648.
- benzoylacetate, action of diazo-benzene on, i, 157.
- benzoylbenzeneazocyanacetate, i, 466.
- benzoyl-*nor-r*-ecgonine, i, 537.
- benzoylsalicylate, i, 66.
- β -benzoxyisocrotonate, i, 628.
- benzuramidobutyrate, i, 645.
- benzuramidocrotonate, i, 645.
- benzuramidofumarate, i, 648.
- benzuramidomaleate, i, 648.
- benzylglutamate, TRANS., 259.
- benzylidenediacetoacetate, action of hydrogen chloride on, i, 419.
- benzylidenedihydrocollidinedicarboxylate, i, 647.
- bromhydroxylutidinedicarboxylate, i, 555.
- bromisodehydracetate, action of ammonia on, i, 555.
- Ethyllic bromodimethyl- α -pyridonecarb-oxylate, i, 403.
- α -bromopropionate, action of sodium nitrite on, i, 65.
- *m*-bromosalicylate, i, 66.
- bromylimidocarbonate, i, 305.
- butanetracarboxylate, preparation of, i, 693.
- camphanate, i, 526.
- campholytate, TRANS., 498.
- camphorates, action of phenylhydrazine on, i, 600.
- carbacetoacetate, i, 306.
- carbethoxyacetoacetate, i, 68.
- β -carbethoxyacrylate, i, 629.
- β -carbethoxyisocrotonate, i, 629.
- carbethoxymethylacetoacetate, i, 70.
- chloride, action of bromine on, i, 62.
- chloro-formate, molecular weight in the liquid state, TRANS., 1100.
- — perchloro-, i, 188.
- chloroxalacetate, hydrolysis of, i, 11.
- cinnamaluramidocrotonate, i, 647.
- *p*-cresoxypropylmalonate, i, 10.
- cuminaluramidocrotonate, i, 646.
- cuprosalicylate, i, 66.
- cyanacetate, synthesis with the aid of, i, 305.
- cyanide, condensation of, with ethylic succinate, i, 397.
- — α -dichlor-, action of hydrogen chloride and hydrogen bromide on, i, 121.
- — dimolecular α -dichlor-, i, 222.
- — — action of ammonia on, i, 122.
- γ -cyanopropylmalonate, i, 9.
- cyanosuccinate, syntheses with the aid of, i, 305.
- diacetomalonate, i, 69.
- diacetyl-glycerate, TRANS., 1422.
- dibenzoylcarbamate, i, 410.
- dibromogallate, i, 343.
- dibromosalicylate, i, 66.
- dibromosuccinate, action of sodium ethoxide on, i, 142.
- *o*-dicyanobenzylecyanacetate, i, 17.
- diethylsalicylate, i, 66.
- diethylsuccinosuccinate, i, 258.
- dihydrocollidinedicarboxylate, ketone from, i, 667.
- dihydromethylketolyl- β -keto-propionate, i, 521.
- dihydroxybrassidate, i, 393.
- diiodocrotonate, i, 397.
- diiodofumarate, i, 397.
- diisopropylsuccinosuccinate, i, 258.
- 2:2'-dimethylbenzimidazole-3'-acetate, i, 433.

- Ethylac oxalacetate, condensation products of the hydrazone of, i, 367.
 — oxalodiacetate, action of hydrazine hydrate on, i, 429.
 — oxalylphenylhydrazine, action of ethyl chlorocarbonate on, i, 554.
 — oxide, molecular weight of, in the liquid state, TRANS., 1100.
 — oxomalonate, i, 193.
 — phenylbenzylhydrazinesuccinate, i, 371.
 — phenylcyanopyruvate, i, 37.
 — phenylhydroxyparacetate, i, 714.
 — phenylpyrazolonecarboxylate, TRANS., 879.
 — phthalocyanacetate, i, 467.
 — potassium dimethylmalonate, electrolysis of, i, 394.
 — — sebate, electrolysis of, i, 895.
 — propionate, vapour pressure, molecular volume and critical constants of, TRANS., 1226.
 — pyrazoline-3 : 5-dicarboxylate, i, 431.
 — pyrazolone-3-carboxylate, i, 180.
 — pyridazolone-3-carboxylate, i, 732.
 — pyrotartrate, ortho-, i, 252, 307.
 — pyruvate and the product of its condensation with hydrogen chloride, i, 552.
 — — *m*-chlorophenylhydrazone, TRANS., 872.
 — — *o*-chlorophenylhydrazone, TRANS., 868.
 — — *p*-chlorophenylhydrazone, TRANS., 873.
 — ricinate, i, 456.
 — salicyluramidocrotonate, i, 646.
 — silicate, action of ethyl chlorocarbonate on, i, 67.
 — — catalytic action of aluminium chloride on, i, 62.
 — — constitution of, i, 67.
 — — sodiobenzeneazocyanacetate, i, 466.
 — — sodiocyanacetate, action of chlorides of bibasic acids on, i, 143.
 — — sodiocyanopyruvate, i, 396.
 — — — action of diazobenzene chloride on, i, 396.
 — — — sodiosalicylate, i, 66.
 — — sodium camphorate, ortho-, electrolysis of, TRANS., 495.
 — — — thiosulphate, i, 416.
 — — succinate, action of sodium ethoxide on, i, 686.
 — — — and formate, condensation of, i, 192.
 — — succinodicyanacetate, i, 143.
 — — thiocarbamates, physiological action of the two isomeric, ii, 584.
- Ethylac thiocarbimide, molecular weight of, in the liquid state, TRANS., 1100.
 — — thiocyanate, molecular weight of, in the liquid state, TRANS., 1100.
 — — thionylmetamidobenzoate, i, 517.
 — — *p*-toluate, amido-, i, 533.
 — — *p*-toluenesulphonate, i, 270.
 — — trichloropyruvate, i, 308.
 Ethylideneacetone, i, 8.
 Ethylideneacetophenone, trichlor-, i, 390.
 Ethylidenediethylsulphone, behaviour of, in the organism, ii, 289.
 Ethylideneorthamidobenzyl alcohol, i, 23.
 — — — trichlor-, i, 23.
 Ethylidenepropionic acid, i, 392.
 Ethylidene chloride, magnetic rotation of, ii, 442.
 — — — heat of vaporisation of, ii, 446.
 Ethylisoamylthiourea, TRANS., 323.
 Ethylisobutylthiourea, TRANS., 320.
 Ethylisoeugenol, thermochemistry of, ii, 154.
 Ethylisonitrosocamphor, i, 660.
 Ethylisopropylcarbinol, i, 124.
 Ethylisopropylcarbinyl acetate, i, 124.
 — — iodide, i, 124.
 Ethylisopropylchloromethane, i, 124.
 Ethylitaconic acid, i, 195.
 Ethylmesaconic acid, i, 195.
 Ethylmethylpropylethyleneglycol, i, 545.
 α -Ethyl-naphthalene, chlorination of, i, 422.
n-Ethyl-naphthophenazonium hydr-oxide, i, 282.
 — — iodide, i, 283.
 β -Ethyl-naphthylenediamine, i, 284.
 Ethylorthophenylenediamine, oxidation of, i, 199.
o-Ethylorthotoluamide, i, 532.
 — — chloro-, i, 532.
 Ethylorthotoluidine, nitro-, i, 77.
p-Ethylorthotolylenediamine, i, 285.
 Ethyl- α -oxynaphthindone, i, 338.
 Ethylphenanthridone, i, 722.
 Ethylparatoluamide, bromo-, i, 533.
 Ethylparatoluidineorthosulphonic acid, i, 584.
 Ethylphenylketoxime, i, 499.
 Ethylpropylcarbinyl hydrogen sulphate, i, 495.
 α -Ethylpropyltriphenylpseudodithiobiuret, i, 576.
 β -Ethylpropyltriphenylpseudodithiobiuret, i, 576.
 Ethyl- α -picoline, brom-, i, 43.
 β Ethylpiperidine aurochloride, i, 602.
 2-Ethyl- β -pyrazole-4 : 2-dicarboxylic acid, i, 281.
 1-Ethyl-2 pyridone, i, 279.

1-Ethylpyrroline ferrocyanide, i, 602.
 Ethylresorcyglyoxylic acid, i, 413.
 Ethylresorcylic acid, i, 413.
 Ethyltartronic acid, i, 553.
 Ethylthionamic acid, i, 505.
 Ettringite from Tombstone, Arizona, ii, 536, 578.
 Eucalyptol, i, 726.
Eucalyptus globulus, essence of, i, 726.
 Eucalyptus oil, crystalline dihydrochloride from, i, 223.
 Eugenol, thermochemistry of, ii, 154.
 Eugenolcinnamic acid, i, 643.
 Eurhodoles from dihydroxydiketotetrahydronaphthalene, i, 356.
 Evaporation, rate of, determination of molecular weight from, ii, 261.
 Excretion of phosphoric acid, effect of work on, ii, 583.
 Exercise and respiratory interchange, ii, 579.
 Expansion, thermal, of certain paraffins and paraffin derivatives, TRANS., 273.
 — of liquids, determination of, TRANS., 262.
 Explosion, temperature of, ii, 257, 258.
 Explosives, ii, 409.
 Extraction apparatus for liquids, ii, 567.
 Exudations, proteids in, ii, 334.

F.

Fabrics, estimation of silk in, ii, 611.
 — textile, hygroscopic properties of, ii, 368.
 Falkenhaynite, ii, 576.
 Fat analysis, new method of, ii, 604.
 — estimation of, in bread, ii, 197.
 — estimation of, in milk, ii, 55, 101, 251, 252, 308, 396, 559, 601.
 — estimation of, in milk by Babcock's method, ii, 251.
 — estimation of, in milk with Demichel's lactobutyrometer, ii, 55.
 — neutral, detection and estimation of, in mineral oils, ii, 604.
 — of milk, influence of sugar on the constitution of, ii, 27.
 — origin of, from proteid in the body, ii, 327.
 — wool-, detection of foreign fats in, ii, 351, 397.
 Fats, absorption of, in the organism, ii, 24.
 — analysis of, ii, 310.
 — and oils, iodine absorption of, ii, 309.
 — Hübl's iodine numbers for, ii, 103.
 — saponifiable and unsaponifiable, analysis of mixtures of, ii, 102.
 Fatty series, substitution in, i, 449.

Feeding experiments with sunflower cake on cows, ii, 328.
 Fenchone, action of phosphoric anhydride on, i, 597.
 Fenchone-derivatives, active and inactive, i, 106.
 Fenchylamine derivatives, rotatory powers of, i, 725.
 Ferment, diastatic, in blood, ii, 581.
 — in *Penicillium glaucum* resembling emulsin, i, 744.
 — lævoholactic, of the pear, morphology of, TRANS., 1263.
 — organised, from cherry tree gum, ii, 180.
 Fermentation, alcoholic, of Jerusalem artichokes with pure yeast, ii, 482.
 — ammoniacal, in soils, ii, 291.
 — butyl-alcoholic, ii, 586.
 — chemical changes in tobacco during, ii, 592.
 — influence of antiseptics on, ii, 32.
 — of dextrose, rhamnose, and mannitol by a lævoholactic ferment, TRANS., 1263.
 — of glucose, formation of citric acid in, ii, 591.
 — of manure, ii, 182.
 Ferments, diastatic and peptone-forming, in the organism, influence of carbonic anhydride on, ii, 475.
 — fat-decomposing and glucoside-decomposing, relations between, ii, 85.
 — formed and unformed, difference between, ii, 31.
 — hydrolytic, behaviour of, in the organism, ii, 329.
 Ferric chloride, action of liquid ammonia on, ii, 470.
 — action of water on, ii, 405.
 — action of water vapour on, ii, 280.
 — and ammonium chloride, mixed crystals of, ii, 280.
 — hydrates of, ii, 119.
 — chlorobromide, ii, 377.
 — fluoride, ii, 122.
 — non-dissociation of, in solution, ii, 316.
 — hydroxide, crystalline, ii, 169.
 — iron, distribution of, between oxalic and hydrochloric acids, ii, 405.
 — oxalate, action of water on, ii, 405.
 — heat of formation of, ii, 405.
 — oxide, action of a high temperature on, ii, 167.
 — amorphous hydrated, ii, 169.
 — estimation of, in soils and rocks, ii, 243.
 — ignited, dissolution of, ii, 468.
 — phosphate, ii, 573.
 — salts, action of zinc on, ii, 468.

- Ferric salts, decomposition of oxalic acid by, ii, 405.
 ——— reaction of, with thiocyanates, i, 122, 185, 289, 290.
 ——— titration of, ii, 193.
 Ferroaluminium, analysis of, ii, 96.
 ——— estimation of aluminium in, ii, 48, 96, 243, 391.
 Ferrocchrome, analysis of, ii, 96.
 Ferrosilicon, analysis of, ii, 96, 304.
 Ferrotitanium, analysis of, ii, 96.
 Ferrotungsten, analysis of, ii, 96.
 Ferrous alkali sulphates, crystallography of, TRANS., 365.
 ——— fluoride, ii, 122.
 ——— sulphate, employment of in agriculture, ii, 142.
 Fever, influence of, on the glycogen of the liver, ii, 541.
 Fibre, estimation of, in foods, ii, 611.
 Fibrin, solutions of, i, 743.
 Fibrin-peptone, i, 235.
 Fibrin, preparation and properties of, i, 183.
 ——— rotatory power of, i, 60.
 Filter, Gooch, use of the, ii, 90.
 Filters, clay, ii, 368.
 Fire-damp, detection of small quantities of, ii, 487.
 Fisetol, constitution of, i, 413.
 Fishes, respiration in, ii, 81.
 Fish-guano, analysis of, ii, 389.
 Flames, electrical conductivity of, ii, 563.
 ——— of metallic compounds, spectra of, ii, 401.
 Flesh, organic bases of the juice of, i, 55.
 Flour, wheat-, detection of, in rye-flour, ii, 250.
 Flowers of *Tagetes glandulifera*, i, 623.
 Fluavil, i, 225.
 Fluids, effect of gravity on, at the critical point, ii, 112.
 Fluoran, action of phenylhydrazine on, i, 473.
 Fluorescein bisphenylcarbamate, i, 420.
 ——— of camphoric anhydride, TRANS., 961.
 Fluoresceinanilide, i, 721.
 ——— dimethyl ether, i, 721.
 Fluorescein-group, i, 220.
 Fluoresceins, origin of colour in, PROC., 1893, 53.
 Fluorescence, origin of, TRANS., 243; PROC., 1892, 189; 1893, 52.
 Fluorides, double, ii, 373.
 ——— Effront's method for the purification and preservation of yeast by, ii, 481.
 Fluorine compounds, electrical conductivity and freezing point of aqueous solutions of, ii, 315.
 Fluorine compounds, in the organism, ii, 23.
 ——— estimation of, in combustible gases, ii, 488.
 ——— estimation of, in the ash of plants, ii, 234.
 ——— in bones and teeth, ii, 81.
 ——— in fossil wood, ii, 76.
 ——— physical constants of, ii, 204.
 Fluoroxhypomolybdic acid, salts of, ii, 124.
 Fluoroxmolybdic acid, salts of, ii, 124.
 Fluoroxypermolybdic acid, salts of, ii, 124.
 Fodder plants, Swedish, ii, 592.
 Fœtal urine, ii, 428.
 Folgerite not a distinct species, ii, 535.
 Formaldehyde, i, 389.
 ——— action of β -naphthol on, i, 100.
 ——— action of, on nitrosodimethylaniline, i, 509.
 ——— assimilation of, by green plant cells, ii, 32.
 ——— condensation of, with naphthols, i, 172.
 ——— detection and estimation of, ii, 439.
 Formates, metallic, electrolysis of, ii, 191.
 Formazyl hydride, i, 83, 85.
 ——— methyl ketone, i, 84, 157.
 ——— ——— metallic derivatives of, i, 159.
 ——— ——— phenylhydrazone, i, 158.
 Formazylazobenzene, i, 83, 85, 156.
 Formazylcarboxylic acid, i, 82, 85.
 Formazyl-compounds, synthesis of, by the action of diazobenzene on hydrazones, i, 156.
 Formazylphenyl, i, 82, 156.
 Formic acid, molecular weight of, in the liquid state, TRANS., 1103.
 Formonaphthalide, nitration of, PROC., 1893, 8.
l-Formylmenthylamine, i, 724.
r-Formylmenthylamine, i, 725.
 Food, influence of increased or diminished consumption of, on digestion and resorption, ii, 132.
 Foods, detection of horse flesh in, ii, 312.
 ——— estimation of fibre in, ii, 611.
 Franckeite from Bolivia, ii, 576.
 Freezing point and electrical conductivity of aqueous solutions of fluorine compounds, ii, 315.
 ——— of dilute solutions of sodium chloride, ii, 447, 565.
 ——— points of solutions of sulphuric acid, ii, 262.
 ——— of solvents, lowering of, in strong solutions, TRANS., 999.
 ——— of very dilute solutions, ii, 263, 365, 366, 447, 565.

Friedelite, from the Harstig Mine, Sweden, ii, 420.
 — from the Sjö Mine, Sweden, ii, 130.
 Frogs, phloridzin diabetes in, ii, 480.
 — winter, glycogenic function in, ii, 218.
 Fulminates, structure of, i, 494.
 Fulminic acid and its derivatives, i, 542.
 Fumaranilide, diiodo-, i, 397.
 Fumaric acid and maleic acid, isomerism of, i, 193.
 — — chloro-, alleged optical activity of, i, 250.
 — — compounds of, with aromatic amines, i, 264.
 — — diiodo-, i, 397.
 — — sp. gr. of, i, 11.
 Fungi, occurrence of trehalose in, ii, 337.
 Funnel, hot jacket for, ii, 268.
 Furfuralhydrazone, estimation of, ii, 556.
 β -Furfurallevulinic acid, i, 254.
 Furfuran- β -sulphonic acid, *aa*-chloro-bromo-, i, 314.
 Furfuronitrile, $\beta\delta$ -dibromo-, i, 313.
 Furfurylic acetate and benzoate, i, 311.
 — alcohol, i, 311.
 — amylc ether, i, 311.
 — ethylic ether, i, 311.
 — methylic ether, i, 311.
 — propylic ether, i, 311.
 β -Furfuryllevulinic acid, i, 255.
 δ -Furfuryllevulinic acid, i, 255.
 Furnace, electrical, ii, 314, 507.
 Furyldimethylpyrimidine, i, 735.
 Fusel oil, alcohols in, i, 63.
 — — preparation of active amyl alcohol and active valeric acid from, TRANS., 1130.

G.

Gadolinite earths, fractionation of, with aniline and aniline hydrochloride, ii, 376.
 — — fractionation of, with potassium chromate, ii, 375.
 — — metals, separation of, ii, 283.
 Gadolinium oxide, molecular weight of, ii, 211.
 β -Galactan in leguminous seeds, ii, 139.
 Galactose, behaviour of, in diabetics, ii, 177.
 — benzoate, i, 186.
 — birotation and hydrazone formation of, i, 126.
 — decomposition of, by calcium hydroxide, i, 546.
 — physiological action of, ii, 585.
 Galactosephenylhydrazone, specific rotatory power of, i, 126.
 Galena, analysis of, ii, 493.
 — — artificial production of, ii, 214.
 Gallanilide, i, 167.
 — and its triacetyl and tribenzoyl derivatives, i, 412.
 — — metallic derivatives of, i, 638.
 Gallein benzenesulphonates, i, 478.
 Gallic acid, bromo- and its derivatives, i, 583.
 — — derivatives of, i, 343.
 — — dibromo-, and its salts, i, 269.
 Gallic-blue, constitution of, i, 510.
 Gallocyanin, action of aniline on, i, 44.
 Gallocyaninanilide, i, 45.
 Galvanic cells, gold and platinum, electromotive forces of, ii, 149.
 — combinations, E.M.F. of, ii, 150.
 Garlic, essential oil of, i, 103.
 Garnet, artificial production of, ii, 129.
 Gas, coal-, estimation of nitrogen in, ii, 296.
 — — probable presence of iron carbonyl in certain, ii, 73.
 — evolution apparatus, continuous, ii, 65.
 — exchange, influence of light on, ii, 131.
 — purifiers, estimation of cyanogen in the spent materials from, ii, 50.
 Gases, combustible, estimation of fluorine in, ii, 487.
 — densities of, ii, 453, 514.
 — dissolved in water, apparatus for extracting, ii, 432.
 — dry, combination of, PROC., 1893, 165.
 — elasticity of, ii, 9.
 — electrical conductivity of, ii, 563.
 — mixed, temperature of explosion of, ii, 202, 257, 258.
 — of blood during anaesthesia, ii, 540.
 — rarefied, separation and striation of, under the influence of the electric discharge, ii, 253.
 Gastric juice, behaviour of hydrochloric acid to albumin in relation to the chemical investigation of, i, 233.
 — — estimation of free hydrochloric acid in, i, 233, 433.
 Gas-volumeter, Lunge's, new accessory to, ii, 229.
 — new, ii, 230.
 Gas-volumeters, improvements in, ii, 41.
 Geissospermene, i, 446.
 Gelatin, estimation of, in commercial peptones, ii, 147.
 Gelsemine, i, 614.
 Gelseminine, i, 492, 614.
 — methiodide, i, 493.

- Gelsemium sempervirens*, alkaloïds of, i, 614.
- Geoffroya barks, i, 182.
- Geoffroyine, i, 182.
- Geraniol, i, 664.
- Ginger, genuine and exhausted, discrimination between, ii, 611.
- Glass, action of ammonium hydrogen sulphate on, ii, 280.
- lime soda, graphochemistry of, ii, 119.
- Glauconite from Hanover Co., Virginia, ii, 287.
- Globulin, crystalline, occurring in human urine, ii, 290.
- respiratory, in the blood of chitons, i, 60.
- Globulins, crystalline, i, 380 ; ii, 290.
- of kidney and liver cells, ii, 134.
- Glucina, preparation of, from beryl, TRANS., 909.
- Glucose, birotation of, i, 545.
- detection and estimation of, by means of phenylhydrazine, ii, 555.
- formation of citric acid in the fermentation of, ii, 591.
- pentacetyl derivatives of, i, 246.
- See also Dextrose.
- Glucoseoxime, i, 293.
- Glucosephenylhydrazone, specific rotatory power of, i, 126.
- Glucosides of the Convolvulaceæ, i, 423.
- Glue making, valuation of hide clippings for, ii, 610.
- Gluten, pre-existence of, in wheat, ii, 292.
- Glyceric acid, active, densities, molecular volumes, and molecular rotations of ethereal salts of, TRANS., 526.
- — active, normal, butyl, heptyl, and octyl salts of, TRANS., 1410.
- — active and inactive, salts of, TRANS., 296, 511.
- — isotrichloro-, i, 308.
- — rotatory power of ethereal salts of, ii, 561 ; TRANS., 1414.
- Glycerol, bye-products of the action of sodium hydroxide on, i, 246.
- derivatives of, i, 3.
- diallyl ether of, i, 384.
- estimation of, by Benedikt and Zeigmondy's method, ii, 51.
- estimation of, by oxidation, ii, 247.
- estimation of, in wine, &c., ii, 247, 248.
- from soap works, estimation of sodium sulphite, sulphide, and thio-sulphate in, ii, 348.
- nitrate, estimation of nitrogen in, ii, 184.
- oxidation of, in acid solution, ii, 247.
- Glycide, properties of, i, 4.
- Glycogen, i, 386.
- benzoate, i, 187.
- estimation of, ii, 601.
- form of occurrence of, in the body, ii, 581.
- hepatic, influence of fever on, ii, 541.
- in blood and pus, ii, 541.
- occurrence of, in blood, ii, 176, 333.
- origin of, in the organism, ii, 585.
- preparation of, from liver and muscle, i, 618.
- specific rotatory power of, i, 619.
- Glycogenic function in winter frogs, ii, 218.
- Glycol from trimethylacetaldehyde, i, 543.
- molecular weight of, in the liquid state, TRANS., 1103.
- Glycolaldehyde, i, 7.
- Glycollic acid, heat of combustion of, ii, 6.
- — thio-, behaviour of, in the organism, ii, 289.
- Glycollide and its homologues, i, 250.
- Heintz's, i, 306.
- Glyoxaline, formula of, i, 438.
- Glyoxalinedicarboxylic acids, i, 281.
- Glyoxalphenylosazone, i, 188.
- Glyoxime peroxide, dibromo-, i, 494.
- Glyoxylic acid, constitution of, i, 141.
- — heat of combustion of, ii, 6.
- Goats' milk and its detection in admixture with cows' milk, ii, 396.
- Goats, resistance of, to the action of morphine, ii, 335.
- Gold, action of bromine on, ii, 284, 474.
- action of chlorine on, ii, 474.
- action of hydrochloric acid on, under pressure, ii, 169.
- action of silicon on, ii, 474.
- and tin, compounds of, ii, 74.
- bullion assay, limits of accuracy attained in, TRANS., 700.
- containing palladium from the Caucasus, ii, 475.
- crystals containing mercury, ii, 534.
- detection of, ii, 192.
- detection of, in dilute solution, ii, 245.
- dissolution of, in a solution of potassium cyanide, TRANS., 724.
- double halogen salts of, ii, 126, 474.
- effect of other metals on the volatility of, TRANS., 722.
- estimation of, by electrolysis, ii, 305.

- Gold, losses of, in bullion assaying, TRANS., 710.
 — metallic, volatilisation of, TRANS., 714.
 — purple, variety of, soluble in water, ii, 575.
 — refining of, ii, 17.
 — volatilisation of, in the electric arc, ii, 508.
Granulobacter butylicum, ii, 586.
 Graphite and graphitite, ii, 320.
 — behaviour of, with nitric acid, ii, 414.
 — in blue earth from the Cape, ii, 285.
 — intumescent, ii, 320.
 Graphochemistry of compounds C_nH_mOp , i, 185.
 Gravity, effect of, on fluids at the critical point, ii, 112.
 — influence of, on the concentration of solutions, ii, 315.
 Griess-Sandmeyer reaction, PROC., 1892, 199.
 Guaiacol, i, 320.
 — molecular weight of, in the liquid state, TRANS., 1101.
 Guanidine, nitro-, thermochemistry of, ii, 363.
 — nitroso-, i, 389.
 Guanine and its derivative, i, 309.
 Guano, fish-, analysis of, ii, 389.
 Gum arabic, i, 294.
 — molecular mass of, i, 7.
 — preparation of mucic acid from, i, 628.
 — benzoïn from Siam, i, 666.
 — from Sumatra, constituents of, i, 480, 481.
 — cherry tree, organised ferment from, ii, 180.
 — lac, wax of, i, 548.
 — wood-, parent substance of, i, 128.
 Gums, polarimetric examination of, ii, 502.
 Gun-cotton, analysis of, ii, 197.
 Gunpowder, graphochemistry of, ii, 115.
 Gutta, i, 225.
 Gutta-percha, i, 224.
 Gypsum, artificial, ii, 577.

H.

- Hæmochromogen, i, 447.
 — action of carbonic oxide on, i, 448.
 Hæmatin, composition of, i, 743.
 — reduced, i, 447.
 — action of carbonic oxide on, i, 448.
 Hæmatite and martite iron ores in Mexico, ii, 325.

- Hæmatite as a sublimation product, ii, 18.
 Hæmatites, Clinton, ii, 76.
 Hæmatoporphyrin, composition of, i, 743.
 — in urine, ii, 178, 480.
 Hæmoglobin which contains phosphorus, i, 616.
 Halogens and the cyanogen radicle, mechanical comparison between, i, 1.
 Hardness of water, estimation of, ii, 347.
 Haricots, assimilation of nitrogen by, ii, 33.
 Hauchecornite, a nickel bismuth sulphide, ii, 418.
 Hauyn, synthesis of, ii, 19, 422.
 Hauyn-group, synthesis of minerals of, ii, 19.
 Heart, action of inorganic salts on the, ii, 221.
 — embryonic, physiology of the, ii, 424.
 Heat, laws of the expansion of liquids by, ii, 152.
 — of combustion of camphor, ii, 108.
 — of chlorine compounds, ii, 5.
 — of gaseous hydrocarbons, ii, 444.
 — of glycollic and glyoxylic acids, ii, 6.
 — of organic compounds, ii, 59.
 — of dissociation of some acids, ii, 259.
 — of formation of arragonite, ii, 259.
 — of ferric oxalate, ii, 405.
 — of hydration of maleïc anhydride, ii, 108.
 — of ionisation, ii, 357.
 — of vaporisation of hydrogen chloride, ii, 445.
 — of organic compounds, ii, 445.
 — radiant, absorption of, by alum, ii, 5.
 — specific, of boron, ii, 404.
 — of carbonic anhydride, ii, 5.
 — of erythritol and mannitol, ii, 258.
 — of liquid ammonia, ii, 258.
 — of the atoms, ii, 59.
 — of water, ii, 443.
 Heats of formation and temperatures of reaction, relation between, ii, 152.
 Helianthenin, i, 618.
 Helvine, composition of, ii, 422.
 Hemiacetals derived from substituted chloranils, i, 563.
 Heptanaphthene from Caucasian petroleum, i, 151.
 — from perseitol and from resin oil, 635.

- Heptanaphthenecarboxylic acid, oxidation of, i, 209.
 Heptanaphthenic acid, i, 93, 209.
 Heptane, tertiary nitro-, i, 243.
 Heptoglycerol, i, 144.
 Heptolactone, TRANS., 1332.
 — constitution of, TRANS., 1330.
 — preparation of, TRANS., 1337.
 — synthesis of, TRANS., 1336.
 Heptylic glycerate, active, TRANS., 1412.
 1 : 4-Heptylphenol, i, 216.
 Herderite from Hebron, Maine, ii, 76.
 Hermerythrin, i, 59.
 Heulandite from Brazil, ii, 422.
 Hexahydrobenzene, i, 150, 255.
 — bromo-, i, 255.
 Hexahydrobenzoic acid, i, 34, 93, 209.
 — — bromo-, i, 35.
 — — synthesis of, i, 695.
 Hexahydroisophthalic acid, i, 713.
 Hexahydronicotine and its derivatives, i, 489.
 Hexahydrophenol, i, 255.
 Hexahydrotoluene, i, 151.
 Hexametaphosphates, ii, 569.
 Hexamethyleneamine salts, i, 298.
 Hexamethyleneamine-diccatechol, i, 298.
 Hexamethyleneamine-dipyrogallol, i, 298.
 Hexamethyleneamine-diresorcinol, i, 298.
 Hexamethyleneamine-eugenol, i, 299.
 Hexamethyleneamine-phloroglucinol, i, 299.
 Hexamethyleneamine-quinol, i, 298.
 Hexamethyleneamine-triphenol, i, 298.
 Hexamethylenecarboxylic acid, synthesis of, i, 695.
 Hexamethylrosaniline-violet, action of ammonia on, i, 640.
 Hexamethylstilbene, i, 271.
 — bromide, bromo-, i, 271.
 Hexamethyltriamidophenylacridine, i, 470.
 Hexamolybdoperiodic acid, salts of, ii, 123.
 Hexane, critical constants of, ii, 446.
 — heat of vaporisation of, ii, 446.
 — magnetic rotation of, ii, 442.
 — tertiary nitro-, i, 243.
 Hexethylic ethanehexacarboxylate, i, 630.
 Hexyl palmityl ketone, TRANS., 463.
 — — — oxime, TRANS., 463.
 Hexylaticonic acid, i, 692.
 Hexylbenzene, i, 635.
 Hexyleanacrylic acid, i, 455.
 Hexylene, critical temperature of, ii, 446.
 — dioxide, i, 3.
 — glycol oxide and its derivatives, i, 3.
 — heat developed by the union of bromine with, ii, 444.
 Hexylene, heat of vaporisation of, ii, 446.
 — magnetic rotation of, ii, 442.
 α -Hexylene, normal, condensation of, with benzene, i, 635.
 Hexylic acid, normal, preparation of, i, 687.
 Hexylic alcohol, supposed secondary, from mannitol, i, 246.
 2-Hexyl- β -pyrazoledicarboxylic acid, i, 281.
 Hide clippings, valuation of, for glue-making, ii, 610.
 Hippuraldehyde, i, 300.
 Hippuric acid, condensation of, with phthalic anhydride and with benzaldehyde, i, 580.
 Hippurylphenylbuzylene, i, 463.
 Hofmann Memorial addresses, PROC., 1893, 132.
 Holmium chloride, anhydrous, ii, 466.
 — oxide, complex nature of, ii, 466.
 Homoacetopiperone, i, 262.
 α -Homoeatropine, i, 426.
 Homocatechol, action of sulphuric acid on, i, 637.
 — ethers of, i, 258.
 Homocatecholsulphonic acid, i, 638.
 β -Homochelidonine, i, 490.
 γ -Homochelidonine, i, 490.
 Homocinchonine, i, 678.
 Homologous compounds, boiling points of, PROC., 1893, 145.
 Homomethylene-blue, i, 77.
 Homosalicylide, ortho- and para-, i, 166.
 Homoterephthalic acid, i, 467.
 — — nitro-, i, 212.
 Honey, lime-tree, i, 618.
 Hops, essential oil of, PROC., 1893, 177.
 Hornblende, chemical constitution of, ii, 130.
 Horse, dandruff of the, ii, 585.
 — flesh, detection of, in food, ii, 312.
 Horse's urine, the phosphates of, ii, 30.
 Hyalin, ii, 218.
 Hydantoic acid, thermochemistry of, ii, 360.
 Hydantoïn, thermochemistry of, ii, 359.
 Hydracetylacetone, i, 8.
 Hydrastic acid, i, 117.
 — — dichloro-, i, 117.
 — — methylimide, i, 117.
 — anhydride, i, 117.
 — chloride, dichloro-, i, 117.
 Hydrastimide, i, 117.
 Hydrastine, i, 116.
 — hydrogen tartrate, i, 491.
 — oxidation of, i, 116.
 Hydration, influence of, on solubility, ii, 509.
 Hydrazides, acid, oxidation of, by Fehling's solution, i, 331.

- Hydrazidophenylmethyloxybiazolone hydrochloride, para-, i, 535.
- Hydrazine, estimation of, in hydrazine salts, ii, 605.
- hydrate, action of, on organic halogen compounds, i, 410.
- — reaction of, with the nitro-, nitroso-, and isonitroso-groups, i, 701.
- Hydrazine-derivatives, i, 299.
- Hydrazines, action of chlorides of bi-basic acids on, i, 705.
- action of diazo-compounds on, i, 202.
- aromatic, bromination of, i, 705.
- primary acid, i, 299.
- secondary acid, i, 299.
- 4-Hydrazipyrazolone-3-carbonylhydrazine, i, 730.
- 4-Hydrazipyrazolonecarboxylic acid, lactam of, 730.
- Hydrazobenzene, parachloro-, reduction of, 330.
- om-Hydrazobenzenedicarboxylic acid, i, 210.
- o-Hydrazobenzoic acid, action of acetic anhydride on, i, 200.
- Hydrazobenzyl alcohols, ortho- and para-, i, 201.
- Hydrazoïdes, acid, i, 299.
- Hydrazones, asymmetrical, isomerism of, i, 299.
- — stereochemistry of, i, 207.
- Bulow's test for, i, 461.
- oxidation of, i, 97, 461.
- Hydrindene, i, 518.
- α -amido-, i, 587.
- ethyl ketone and its oxime, i, 717.
- methyl ketone, i, 717.
- phenyl ketone, i, 717.
- synthesis of, i, 716.
- Hydrindenecarboxylamide, i, 717.
- Hydrindenecarboxylic acid, tetrabromo-, i, 717.
- anilide, i, 717.
- chloride, i, 717.
- Hydrindeneethylcarbinol, i, 717.
- Hydrindeneglycol, i, 519.
- Hydrindenemethylcarbinol, i, 717.
- α -Hydrindenesulphonic acid, i, 519.
- β -Hydrindenesulphonic acid, i, 518.
- Hydrindone, new synthesis of, *Proc.*, 1892, 216.
- nitro-, *Proc.*, 1892, 216.
- α -Hydrindone and its derivatives, i, 586.
- β -Hydrindone and its derivatives, i, 587.
- Hydrindoneoxime, *Proc.*, 1892, 216.
- β -Hydrindoneoxime, i, 587.
- Hydrobenzoic acids, i, 33.
- Hydrocaffèic acid in beet leaves, ii, 85.
- Hydrocamphene, liquid isomerides of, i, 523.
- Hydrocarbon $C_{16}H_{12}$, Zincke's, i, 522.
- Hydrocarbon from dihydrochlorossesquiterpene, i, 102.
- Hydrocarbons, aromatic, action of thiocarbimides on, i, 153.
- — condensation of aliphatic alcohols with, i, 634.
- closed-chain, action of bromine on, in presence of aluminium bromide, i, 13.
- coloured, *Proc.*, 1892, 189.
- combinations of, with picric acid and other nitro-compounds, *TRANS.*, 1388.
- derived from dipentene dihydrochloride, *TRANS.*, 292.
- ethylenic, hydration of, i, 61.
- heats of combustion of, ii, 59.
- molecular refractive power of, for infinite wave-length, ii, 57.
- of the benzene series, condensation of, with those of the ethylene series, i, 635.
- unsaturated, action of mercury salts on, i, 450.
- Hydrochloric acid, electrical conductivity of, in various solvents, ii, 151.
- — estimation of, in gastric juice, i, 233; ii, 433.
- — estimation of, in the stomach contents, ii, 86.
- — hydrocyanic acid and thiocyanic acid, estimation of, ii, 503.
- — occurrence of, in the stomach, ii, 540.
- — secretion of, in nervous dyspepsia, ii, 219.
- — See also Hydrogen Chloride.
- Hydrocinnamaldoxime, i, 710.
- Hydroceon and its derivatives, i, 718.
- bromo- and di-bromo-, i, 718.
- Hydrocyanic acid, detection of, ii, 502.
- — detection of, in presence of ferrocyanides, ii, 393.
- — estimation of, in coal gas, ii, 51.
- — formation of, by the action of nitric acid on sugar, &c., i, 617.
- — hydrochloric and thiocyanic acids, estimation of, ii, 503.
- Hydrocyanorosaniline, constitution of, i, 711.
- Hydrodigitolic acid, i, 666.
- Hydrofluoric acid, Effront's method for the purification and preservation of yeast by, ii, 481.
- Hydroisocarbostyryl, i, 530.
- Hydrolysis in aqueous salt solutions, ii, 448.
- Hydromethylketoleparazobenzenesulphonic acid, i, 463.
- Hydropinene, i, 524.
- Hydropyridine compounds, new synthesis of, i, 484.

Hydrogen and chlorine, ignition point of a mixture of, ii, 258.
 — and oxygen, combination of, by pressure, ii, 410.
 — — ignition point of admixed, ii, 203, 257, 208.
 — — relative densities of ii, 10.
 — antimonide, action of, on silver nitrate, ii, 206.
 — arsenide, action of, on silver nitrate, ii, 206.
 — — quantitative conversion of arsenic into, ii, 186.
 — atomic refraction of, ii, 254.
 — bromide, preparation of, ii, 114, 453.
 — — vapour density of, at low temperatures, ii, 66.
 — chloride, density and molecular volume of, ii, 410.
 — — dried, action of, on Iceland spar, ii, 208.
 — — heat of vaporisation of, ii, 445.
 — — hydrates of, *PROC.*, 1893, 45.
 — — magnetic rotation of solutions of, ii, 442.
 — — vapour density of, at low temperatures, ii, 66.
 — — See also Hydrochloric acid.
 — combustion of, in nitrous oxide, ii, 113.
 — density of, ii, 453, 515.
 — fluoride, anhydrous, action of, on alcohols, i, 186.
 — — See also Hydrofluoric acid.
 — iodide, gaseous, decomposition of, by heat, ii, 369.
 — — vapour density of, at low temperatures, ii, 66.
 — nitride, formation of, from aromatic azoimides, i, 90.
 — heat of combustion of, ii, 444.
 — peroxide, action of light, in inducing the formation of, in organic liquids, *TRANS.*, 1109.
 — — conditions which influence the formation of, in urine, *TRANS.*, 1115.
 — — constitution of, ii, 413.
 — — detection of, ii, 233; *TRANS.*, 1110.
 — — estimation of, ii, 86; *TRANS.*, 1110.
 — — formation of, in the spontaneous oxidation of zinc, ii, 412.
 — — molecular weight of, i, 579; ii, 163.
 — — production of, in the electrolysis of aqueous sulphuric acid, ii, 108.
 — — refractive power of, ii, 163.

Hydrogen peroxide, separation of metals by, in alkaline solution, ii, 492.
 — — solutions, ii, 369.
 — — phosphide, action of, on silver nitrate, ii, 207.
 — — decomposition of gaseous, ii, 569.
 — — selenide, absorption of, by selenium, at a high temperature, ii, 457.
 — — sulphide and oxygen, ignition point of a mixture of, ii, 258.
 — — apparatus, ii, 268.
 — — dry, properties of, ii, 164.
 — — oxidation of solutions of, ii, 66.
 — — poisoning by, ii, 83.
 — — production of, by a bacterium in urine, ii, 335.
 Hydroximido-derivatives, i, 474.
m-Hydroxyacetanilide, i, 265.
 Hydroxyacetylaldoxime, *PROC.*, 1893, 77.
 γ -Hydroxy-acids, relative velocity of lactone formation with, i, 71.
 Hydroxyanthraquinolinequinone, i, 670.
 Hydroxyapochinchenic acid, lactone of, i, 377.
 Hydroxyazotetrazole, sodium derivative of, i, 441.
m-Hydroxybenzanilide, i, 265.
 Hydroxybenzeneindone, i, 266.
o-Hydroxybenzylidene-*l*-menthylamine, i, 724.
o-Hydroxybenzylidene-*r*-menthylamine, i, 725.
 Hydroxybenzylideneorthamidobenzylalcohols, ortho- and para-, i, 23.
 ω -Hydroxy- β -bromomethylpyromucic acid, i, 312.
 Hydroxybutyric acid, lactide of, i, 251.
 β -Hydroxybutyric acid in the organism, ii, 428.
 Hydroxycamphoramic acid, i, 526.
 Hydroxycamphoranilic acid, i, 526.
 Hydroxycamphormethylamic acid, i, 526.
 Hydroxycerotic acid, i, 59.
 Hydroxydihydrobenzylidimethylamine platinochloride, i, 114.
 γ -Hydroxydimethylglutaric acid, α -bromo-, lactones of, i, 72.
 Hydroxydimethylxanthone [1:2:4], i, 217.
 β -Hydroxydisulphonaphthoic acid, i, 475.
 Hydroxyethylapochinchenic acid, lactone of, i, 376.
 Hydroxyethylmethylsulphone, i, 459.
 Hydroxyethylsulphoneethylenesulphonic acid, and its lactone, i, 459.
 Hydroxyethylsulphoneethylenesulphonic acid and its lactone, i, 459.

- Hydroxyethylsulphonemethylenesulphonic acid and its lactones, i, 459.
 Hydroxyfumaric acid, i, 630.
 γ -Hydroxyhexahydrobromobenzoic lactone, i, 34.
 α -Hydroxyhydrindene, i, 587.
 Hydroxyhydrindene, amido-, i, 519.
 — chlor-, i, 519.
 Hydroxyhydro- α -naphthaquinone, chlor-, i, 220.
 Hydroxyhydrotropidine platinochloride, i, 114.
 Hydroxyindazole, preparation of, i, 46.
 α -Hydroxyisobutyro- β -naphthalide, i, 53.
 α -Hydroxyisobutyroparatoluidide, i, 53.
 γ -Hydroxyisocaproamide, i, 691.
 γ -Hydroxyisocaproic acid, ammonium salt of, i, 691.
 δ -Hydroxy- γ -isohexylyl lactone, i, 130.
 Hydroxyisodinitroacetone nitrite, i, 303.
 Nt₂-2'-Hydroxyisorosindone, i, 336.
 α -Hydroxy- α -ketoidene, pentachlor-, i, 345.
 Hydroxylamine, action of nitrites on, ii, 318.
 — constitution of, ii, 114.
 — quantitative separations in presence of, ii, 500.
 — salts and nitrites, velocity of reaction between, ii, 160.
 Hydroxylamineacetic acid, i, 501.
 Hydroxy- β -lapachone, bromo-, TRANS., 430.
 Hydroxymetaxylene-carboxylic acid, PROC., 1893, 110.
 1 : 3-Hydroxymethoxyxanthone, i, 218.
 Hydroxymethylenecamphor, ethyl, methyl, and phenyl ethers of, i, 360.
 Hydroxymethylene-compounds, i, 360, 480.
 $\alpha_2\beta$ -Hydroxymethylethylsuccinic acid, i, 146.
 Hydroxymethyl- α -pipecoline platinochloride, i, 114.
 Hydroxymethyl- β -pipecoline platinochloride, i, 114.
 Hydroxymethylpiperidine platinochloride, i, 114.
 ω -Hydroxymethylpyromucic acid, i, 312.
 β Hydroxynaphthamide, i, 221.
 β -Hydroxynaphthaphenazine, i, 356.
 Hydroxy- α -naphthaquinoneanilide, i, 221.
 β -Hydroxynaphthoic acid [m. p. 216°], i, 355, 475, 476.
 — — — constitution of, i, 475, 476.
 β -Hydroxynaphthomethylanilide, i, 221.

p-Hydroxyorthobenzoylbenzoic acid, i, 274.
 — — — dibromo-, i, 719.
 α -Hydroxypentamethylenecarboxylic acid, 1, 557.
 Hydroxyphenanthridine, i, 658.
 o -Hydroxyphenylacrylamide, i, 696.
 Hydroxyphenylglyoxylic acid phenylhydrazone, i, 280.
 Hydroxyplatinodiamine salts, ii, 127.
 Hydroxypropaldehyde, i, 682.
 — propyl derivative of, i, 682.
 α -Hydroxypropaldehyde, dipropyl ether of, i, 383.
 β -Hydroxypyrotartaric acid and its salts, i, 146.
 1-Hydroxyquinoline 1'-benzochloride, i, 485.
 — 1'-benzohydroxide, i, 485.
 — 1'-ethobromide, i, 484.
 — 1'-ethoxide, i, 485.
 3-Hydroxyquinoline, oxidation of, i, 605.
 4-Hydroxyquinoline and its derivatives, i, 485.
 Hydroxyquinolines, i, 484.
 Hydroxyrosindone, i, 335.
 Hydroxyrosinduline, i, 335.
 Hydroxysantogenenic acid, i, 112.
 β -Hydroxysulphonaphthoic acid, i, 356.
 — — amido-, i, 475.
 — acids, i, 475.
 Hydroxytetrahydronaphthylamine, i, 592.
 α -Hydroxy- β -thiotolylisobutyric acid, i, 36.
 Hydroxytropidine platinochloride, i, 114.
 Hydroxytropine platinochloride, i, 114.
 α -Hydroxyvitic acid, action of diazobenzene chloride on, i, 341.
 Hydroxyxanthenes, mono-, constitution of, i, 217.
 — preparation of, from the salts of polyhydric phenols, i, 218.
 Hydurilic acid, i, 149, 405,
 — — — thermochemistry of, ii, 361.
 Hygrineoxime, i, 446.
 Hypobromous and analogous acids, mixed anhydrides of, i, 305.
 Hypochlorites, action of ammonia on, ii, 317.
 — chlorates and chlorides, estimation of admixed, ii, 388.
 — commercial, estimation of free alkali in, ii, 91.
 Hypochlorous and analogous acids, mixed anhydrides of, i, 192, 305.
 Hypiodous acid, amides of, i, 392.
 Hyponitrous acid, preparation of, ii, 318, 372.
 Hypoxanthine, bromo-, i, 736.

Hypoxanthine, constitution of, i, 736.
 Human body, amount of albumin required for, ii, 328.
 Humous substance, relation of the urinary carbohydrates to, ii, 82.
 Hyoscine, i, 679.
 Hyoseyamine, i, 491.

I.

Ice, specific gravity of, ii, 7.
 Idocrase from the Septimer, ii, 578.
 Ignition point, ii, 202, 257, 258.
 Imidazoles, i, 432.
 Imido-ethers, action of hydrazine on, i, 711.
 Inanition, metabolism during, ii, 477.
 Indazole, synthesis of, i, 279.
 Indazolecarboxylic acid, i, 280.
 Indazole-derivatives, i, 46.
m-Indazylbenzoic acid, i, 210.
 Indene, i, 518.
 — dichloro-, i, 519.
 — mono- and di-brom-, i, 717.
 — octochlor-, i, 346.
 — synthesis of, i, 716.
 Indenecarboxylic acid, i, 717.
 Indene-derivatives, conversion of pentene-derivatives into, i, 344.
 Indigo, behaviour of, when heated with alkalis, i, 270.
 Indigo-red, i, 539.
 Indigotin, estimation of, in commercial indigo, ii, 352.
 — thermochemistry of, i, 649.
 — thermochemistry of some derivatives of, i, 649.
 Indigotintetrasulphonic acid, i, 348.
 Indigotintrisulphonic acid, i, 348.
 Indium, spectrum of, ii, 313.
 Indole acids, affinity coefficients of, i, 42.
 — and its derivatives, behaviour of, with respect to Raoult's law, ii, 156.
 — conversion of carbazole into, i, 717.
 Indoles, conversion of, into quinolines, i, 603.
 Indoxazen-derivatives, i, 94, 95, 469.
 Indoxazen-reaction, TRANS., 1346.
 Indoxylazobenzenesulphonic acid, i, 271.
 Induline ammonium base, i, 336.
 Induline-group, i, 333.
 Indulines, relations of safranines to, i, 613.
 Intestine, small, secretion and absorption in the, ii, 582.
 Intestines, putrefaction in the, ii, 137.
 Intravascular coagulation, ii, 541.

Inulase, i, 497.
 Inulin, i, 385.
 — indirect alcoholic fermentation of, i, 497.
 Inversion of sugar by feeble acids, ii, 62.
 Iodates, detection of, in iodides, ii, 183.
 Iodides, detection of iodates in, ii, 183.
 — metallic, solubility of, in methylenic iodide, ii, 378.
 Iodine, absorption of, ii, 309.
 — atomic refraction of, ii, 254.
 — and bromine, estimation of, in presence of chlorine, ii, 42.
 — and chlorine, direct separation of, ii, 183.
 — chlorine, and bromine, detection of, in admixture, ii, 343.
 — — separation of, ii, 183, 295, 595.
 — detection and estimation of cyanogen in, ii, 246.
 — estimation of, in haloïd salts by the action of arsenic acid, ii, 488.
 — estimation of the vapour density of, at various temperatures, ii, 154.
 — gas-volumetric estimation of, ii, 87, 144.
 — heptavalent, complex acids containing, ii, 122.
 — monochloride, ii, 514.
 — preparation of pure, ii, 204.
 — separation of, from bromine and chlorine, TRANS., 1051.
 — solution, preparation of standard, ii, 234.
 Iodine-compounds, physiological action of, ii, 222.
 Iodine-spring in Austrian Silesia, ii, 579.
 Iodoso-compounds, i, 505, 506, 561, 713.
 Iodoxy-compounds, i, 505, 561.
 Iodyl acetamide, i, 392.
 — succinimide, i, 392.
 Ions, colour of the, ii, 510.
 — thermochemistry of, ii, 357.
 Ionisation and electrolytic dissociation, ii, 4.
 Ipecacuanha, estimation of emetine in, ii, 397, 560, 608.
 Ipomeolic acid, i, 482.
Ipomœa pandurata, glucoside of, i, 482.
 — *turpethum*, glucoside of, i, 424.
 Ipomœic acid, i, 482.
 Ipomœin, i, 482.
 Iridium, bisulphide, ii, 380.
 — crystalline form of, ii, 281.
 — electrolytic separation of palladium and platinum from, ii, 97.
 — sulphide, ii, 379.

- Iris germanica*, composition of, ii, 227.
 — — — presence of boron, copper, and lithium in, ii, 227.
- Iron, absorption of, in animals, ii, 23.
 — — — absorption of, in the small intestine, ii, 582.
 — — — action of drugs containing, ii, 427.
 — — — aluminium, and chromium, separation of, ii, 49.
 — — — manganese, zinc, and calcium, separation of, ii, 600.
 — — — analysis of, ii, 499.
 — — — and nickel, supposed new sulphides of, ii, 535.
 — — — and tin, alloys of, ii, 211.
 — — — and tungsten, crystalline alloy of, ii, 170.
 — — — bromoborate, ii, 518.
 — — — carbonyl, probable presence of, in certain illuminating gas, ii, 73.
 — — — chloroborate, ii, 468.
 — — — colorimetric estimation of, ii, 50.
 — — — electrochemical effects on magnetising, ii, 404.
 — — — electrolytic estimation of, ii, 94.
 — — — estimation of, by an iodometric method, ii, 439.
 — — — estimation of carbon in, ii, 45, 491.
 — — — estimation of chromium in, ii, 554.
 — — — estimation of, in bone black, ii, 498.
 — — — estimation of, in spring water, ii, 196.
 — — — estimation of manganese in, ii, 304.
 — — — estimation of oxygen in, ii, 388.
 — — — estimation of phosphorus in, ii, 44, 235, 596.
 — — — estimation of phosphorus in, in presence of arsenic, ii, 554.
 — — — estimation of sulphur in, ii, 389.
 — — — fluorides, anhydrous and crystalline, ii, 122.
 — — — in chlorosis, ii, 427.
 — — — in plants, ii, 484.
 — — — influence of electricity on the carburisation of, by cementation, ii, 527.
 — — — modification of the stannous chloride method of titrating, ii, 499.
 — — — native, of Ovivak, ii, 316, 475.
 — — — oxide, estimation of, in iron and steel, ii, 499.
 — — — passive state of, ii, 16.
 — — — phosphates, natural, formation of, ii, 536.
 — — — pig-, estimation of silicon in, ii, 435.
 — — — possible volatility of, below its melting point, ii, 168.
 — — — pyrites, artificial production of, ii, 214, 576.
 — — — cobaltiferous and nickeliferous from Müsen, ii, 18.
- Iron, separation of, from aluminium, ii, 304, 346.
 — — — sulphites, ii, 456.
 — — — the thiocyanate test for, ii, 438.
 — — — volatilisation of, in the electric arc, ii, 508.
 — — — volumetric estimation of, ii, 492.
 — — — See also Ferric and Ferrous.
- Iron-ore, the Clinton, ii, 76.
- Iron-ores, estimation of phosphorus in, ii, 392.
 — — — of Mexico, ii, 325.
- Isaconitine, TRANS., 443.
 — — — aurochlor-, TRANS., 447.
 — — — conversion of aconitine into, TRANS., 991.
 — — — hydrolysis of, TRANS., 448.
 — — — physiological action of, TRANS., 451.
 — — — reaction of, with auric chloride, TRANS., 447.
 — — — salts of, TRANS., 446.
- Isatide, thermochemistry of, i, 649.
- Isatin, thermochemistry of, i, 649.
- β -Isoamylene, specific volume and thermal expansion of, TRANS., 276.
- o*-Isoamylparaisopropyltoluene, i, 163.
- Isopiole, action of nitrous anhydride on, i, 263.
 — — — diisonitroso-, α - and β -, i, 263.
 — — — diisonitroso-, peroxide, i, 263.
 — — — diisonitrosobrom-, i, 264.
 — — — diisonitrosnitro-, peroxide, i, 263.
 — — — dinitroso-, anhydride, i, 263.
 — — — nitrosite and its anhydride, i, 197.
 — — — thermochemistry of, i, 154.
- Isoapocinchonine, i, 678.
- Isobenzalphthalide, i, 228.
- Isobenzamarone, i, 352.
- Isobutenylphenyl nitrosite, i, 197.
- Isobutylacetamide, α -isonitroso-, i, 503.
- Isobutylamine, action of isobutyllic iodide on, i, 128.
 — — — freezing points of aqueous solutions of, TRANS., 174.
 — — — isobutylthionamate, i, 505.
 — — — thionyl-, i, 504.
- Isobutylbenzene, critical constants of, ii, 446.
 — — — magnetic rotation of, ii, 442.
- Isobutylene, action of nitrosyl chloride on, TRANS., 481.
 — — — hydration of, i, 61.
- Isobutylenic bromide, specific volume and thermal expansion of, TRANS., 288.
- Isobutylic alcohol, magnetic rotation of, ii, 442.
 — — — molecular weight of, in the liquid state, TRANS., 1102.
 — — — velocity of the reaction of acetic anhydride on, ii, 510.

- Isobutylic β -chloropropionate, i, 688.
 — diacetylgllycerate, TRANS., 1425.
 — glycerate (primary), active and inactive, TRANS., 517.
o-Isobutylparaisopropyltoluene, i, 163.
 2-Isobutyl- β -pyrazoledicarboxylic acid, i, 281.
 Isobutyramide, amidoxyl-, i, 503.
 Isobutyramidoacetophenone, i, 531.
 Isobutyric acid, action of phosphoric anhydride on, TRANS., 460.
 — — α -bromo-, action of alcoholic potash on the anilide, toluidides, and naphthalides of, i, 51.
 — — molecular weight of, in the liquid state, TRANS., 1103.
 — aldoxime, PROC., 1893, 78.
 — chloride, action of zinc ethide on, i, 124.
 Isobutyro- α -naphthalide, α -bromo-, i, 53.
 Isobutyro- β -naphthalide, α -bromo-, i, 53.
 Isobutyronitrile, amidoxyl-, i, 503.
 Isobutyroparatoluidide, α -bromo-, i, 53.
 Isobutyrothotoluidide, α -bromo-, i, 53.
 Isocamphoric acid, i, 598.
 Isocamphoronic acid, i, 423.
 Isocaproic acid, molecular weight of, in the liquid state, TRANS., 1104.
 Isocaprolactone, action of sodium ethoxide and ammonia on, i, 699.
 Isocapronitrile, amidoxyl-, i, 503.
 Isocarbostyryl, i, 417.
 Isocinchonine, trihydrido-, i, 181.
 α -Isocinchonine, i, 677.
 — hydrochloro-, i, 677.
 β -Isocinchonine, i, 677.
 β -Isococaic acid, i, 58.
 α -Isoconchinine, i, 677.
 β -Isoconchinine, i, 677.
 Isoconiine, i, 442.
 Isocoumarin-derivatives, synthesis of, i, 366.
 Isocrotonic acid and its derivatives, i, 133.
 — — chlorination and bromination of, i, 132.
p-Isocymyl ethyl ketoxime, i, 163.
 — isobutyl ketone, i, 163.
 — isopropyl ketone, i, 163.
 — propyl ketoxime, i, 163.
 Isoerucic acid, i, 549.
 — — constitution of, i, 551.
 Isoeugenol, thermochemistry of, ii, 154.
 Isoeugenolglycollic acid, i, 643.
 — — nitro-, i, 643.
 Isoflavaniline, i, 531.
 Isoheptolactone, TRANS., 1331.
 Isohexane, specific volume and thermal expansion of, TRANS., 276.
 Isohydroxycamphoric acid, i, 423.
 Isoindole, derivatives of, i, 346.
 Isolauronic acid, i, 363.
 Isomalic acid, synthesis of, i, 145.
 Isomaltose, estimation of, in worts, ii, 601.
 — preparation of, i, 5.
 Isomeric change, PROC., 1892, 213, 214.
 Isomerides, refraction and dispersion equivalents of, ii, 1.
 Isomorphism, ii, 161.
 Isomorphous series, connection between the atomic weight of the contained metals and the magnitude of the angles of crystals of, TRANS., 337.
 Isomuscarine, i, 297.
 Isonichine and its salts, i, 57, 737.
 Isonitroso-compounds, action of hydrazine hydrate on, i, 701.
 Iso-oleic acid, constitution of, i, 551.
 Isopentane, specific volume and thermal expansion of, TRANS., 275.
 Isophthalic acid, nitro-, electrolytic reduction of, i, 567.
 Isoprene, specific volume and thermal expansion of, TRANS., 277.
 Isopropeneketopentamethylene, i, 129.
 Isopropylamine, freezing points of aqueous solutions of, TRANS., 167.
 — hydrates of, TRANS., 169.
 Isopropylbenzene, critical constants of, ii, 446.
 — magnetic rotation of, ii, 442.
 — parachloro-, i, 562.
 — thermochemistry of, i, 562.
 Isopropylbenzylideneorthamidobenzyl alcohol, i, 24.
 β -Isopropylglutaric acid, synthesis of, TRANS., 1344.
 Isopropyllic alcohol, hydrates of, i, 291.
 — — magnetic rotation of, ii, 442.
 — — molecular weight of, in the liquid state, TRANS., 1102.
 — diacetylgllycerate, TRANS., 1424.
 — glycerate, active and inactive, TRANS., 514.
 — nitrite, i, 382.
 Isopropylorthamidobenzyllic alcohol, i, 38.
 1 : 4-Isopropylphenol, i, 215.
 Isopropylphenylglycollic acids, stereoisomeric, i, 212.
 2-Isopropyl- β -pyrazoledicarboxylic acid, i, 281.
 Isopropyltoluene, thermochemistry of, i, 562.
 Isopropyltoluidinesulphonic acid, i, 584.
 Isorosindulines, i, 333.
 Isorottlerin, TRANS., 988.
 Isoquinoline, amido- [1 : 2' or 4 : 2'], i, 608.
 Isoquinoline, amido-, and its derivatives, i, 366.

Isoquinoline and its derivatives, physiological action of, ii, 585.
 — brom-, and its derivatives, i, 366.
 — dinitro-, and its derivatives, i, 366.
 — formation of, i, 427.
 — new synthesis of, i, 607, 608.
 — nitro- [1 : 2' or 4 : 2'], i, 608.
 — nitro-, and its derivatives, i, 366.
 Isoquinoline-derivatives, i, 608.
 — — synthesis of, i, 228, 366.
 Isosafrole, action of nitrous acid on, i, 261.
 — α -diisonitroso-, i, 261.
 — β -diisonitroso-, i, 262.
 — diisonitroso-, anhydride, i, 262.
 — — peroxide, i, 261.
 — — oxidation of, i, 310.
 — isonitroso-, i, 261.
 — nitrosite and its anhydride, i, 197.
 — nitrosochloride, i, 263.
 — thermochemistry of, ii, 154.
 Isosafrolenitrolpiperidide, i, 261.
 Isosantonone, i, 111.
 Isosantononic acid, i, 111.
 Isosuccinic acid, sp. gr. of, i, 11.
 Isothermals for liquids and gases, form of, ii, 152.
 Isothiohydantoïn, i, 405.
p-Isotolytrosinduline, i, 339, 340.
 Isovaleraldehyde, action of malonic acid on, TRANS., 1334.
 Itaconic acids, conversion of, into citraconic acids, i, 190.

J.

Jalapin, i, 225.
 Jalapinic acid, composition of, i, 225.
Jatropha manihot, products of, ii, 430.
 Jaundice, obstructive, ii, 30.
 Josephinite, a new nickel-iron, ii, 75.
 Jute fibre, explosive nitrates from, i, 295.
 — — produced in England, composition of, TRANS., 964.

K.

Kale, analyses of, ii, 293.
 Kamala, constituents of, TRANS., 975.
 — resins from, TRANS., 985, 989.
 — sugar from, TRANS., 990.
 — wax from, TRANS., 987.
 — yellow, crystalline colouring matter from, TRANS., 986.
 Kaolin, formation of, ii, 422.
 Kehoeite, a new phosphate from Dakota, ii, 537.
 Kerasin, i, 235.

Keratohyalin, ii, 218.
 Ketazocamphorquinone, i, 570.
 Ketazophenylglyoxal, i, 570.
 Ketine, i, 486.
 Keto-acids, application of the dynamical hypothesis to, i, 499.
 Ketoamines, action of nitrous acid on, i, 570.
 Ketoethylapocinchene, i, 376.
 Ketoethylhomapocinchene, i, 377.
 Ketohexamethylene, derivatives of, i, 129.
 α -Ketohydrindene, hexachlorodibrom-, i, 346.
 — oetochlor-, i, 346.
 β -Ketohydrindene, i, 280.
 Ketohydroxysantogenenic acid, i, 111.
 — lactone, i, 111.
 Ketohydroxytriphenyltetrahydrobenzene, i, 219.
 Ketoindene, hexachloro-, i, 320, 345.
 Ketomethylpentene, trichlorimido-, i, 259, 560.
 Ketone from ethylic dihydrocollidinedicarboxylate, i, 667.
 — from wood oil, i, 558.
 — obtained from camphor, constitution of, TRANS., 93.
 Ketones, amido-, i, 734.
 — aromatic, i, 163.
 — — alkyl, i, 162, 464.
 — — isonitroso-, behaviour of, towards acetic anhydride and chloride, i, 159.
 — condensation of, with amidophenols and amidophenyl ethers, i, 78.
 — condensation of, with chloral, i, 389.
 — condensation of, with phenols, i, 214.
 — dichloro-, action of potassium carbonate on, i, 391.
 — fatty, preparation of, TRANS., 452.
 — formation of, by the action of agents such as sulphuric acid and zinc chloride on camphor, TRANS., 75.
 — from pimelic and azelaic acids, i, 557.
 — heats of combustion of, ii, 59.
 — isonitroso-, action of chlorine on, i, 464.
 β -Ketonic acids, action of diazobenzene on, i, 156.
 — — chloro-, decomposition of ethylic salts of, with dilute sulphuric acid, i, 11.
 Ketonic compound from tartaric acid, i, 685.
 Ketopentamethylene, derivatives of, i, 129.
 Ketopentamethylene dicarboxylic acid, i, 253.

Ketopentene, dichlorimido-, i, 559.
 — $\gamma\gamma$ -hexachloro-, action of alkalis on, i, 698.
 — tetrachlorimido-, i, 559.
 — trichlorimido-, i, 559.
 Ketopiperazines, i, 53.
 Ketotetrahydronaphthalene, i, 593.
 Ketoximes, i, 499.
 — molecular refraction of, ii, 401.
 Ketoximic acids, formation of inner anhydrides from, i, 583.
 Kidney cells, proteids of, ii, 133.
 — substance, chemistry of the, ii, 27.
 — the work of the, ii, 542.
 Kopp Memorial Lecture, TRANS., 775.
 Kyanidine, derivatives of, i, 735.
 Kylindrite, ii, 576.

L.

Lactic acid, estimation of, in milk, ii, 250.
 — — in blood and urine, ii, 136.
 — — inactive, preparation of sarcos lactic acid from, TRANS., 1028.
 — — resolution of, into its optically active components, TRANS., 1143.
 Lactobutyrometer, Demichel's, ii, 55.
 Lacto-globulin, ii, 134.
 Lactone formation in the case of bibasic γ -hydroxy-acids, relative velocity of, i, 71.
 — from levulinic acid and formaldehyde, i, 628.
 — from pyruvic acid and formaldehyde, i, 628.
 Lactones, action of alcohols on, i, 500.
 — action of alkyl salts on, i, 500.
 — action of phenylhydrazine on, i, 473, 522.
 — heats of combustion of, ii, 59.
 Lactonic acids, heats of combustion of, ii, 59.
 Lactosecarboxylic acid, i, 148.
 Lactoses, identification and estimation of the, in different milks, ii, 502.
 β -Lactylcarbamide, i, 632.
 Lævofenchone, i, 105.
 Lævofenchyl alcohol, i, 106.
 Lævolactic fermentation of dextrose, rhamnose, and mannitol, TRANS., 1263.
 Lævolimonene, oxidation of, TRANS., 293.
 Lævomethoxysuccinic acid, TRANS., 227.
 Långbanite, ii, 421.
 Lapachol and its derivatives, constitution of, TRANS., 1376.
 β -Lapachone, dibromo-, TRANS., 424.
 Lard, analysis of, ii, 101.
 — detection and approximate estimation of cotton seed oil in, ii, 440.
 — detection of heated cotton seed oil in, ii, 603.
Lathyrus sylvestris, analysis of, and of the hay made from it, ii, 547.
 Laudanine, i, 181.
 Lava from Northern California, ii, 578.
 Law of Dulong and Petit, ii, 404.
 Lead ammonium chlorides, ii, 523.
 — — haloïds, ii, 523.
 — — iodide, TRANS., 542.
 — — arsenates, ii, 274.
 — — bromiodide, TRANS., 545.
 — — chloride, compounds of, with pyridine, ii, 465.
 — — chloriodides, TRANS., 544.
 — — detection and estimation of, in tartaric and citric acids, ii, 557, 599.
 — — detection and estimation of minute quantities of, in presence of copper and iron, ii, 242.
 — — detection of, ii, 192, 242, 557, 599.
 — — detection of, in urine, ii, 600.
 — — double haloïd salts of, with cæsium and potassium, ii, 322.
 — — electrolytic estimation of, ii, 94.
 — — electrolytic separation of, from bismuth, ii, 495.
 — — electrolytic separation of mercury and of silver from, ii, 496.
 — — estimation of, ii, 94, 95, 242, 302, 437, 557, 599.
 — — estimation of, in alloys, ii, 95.
 — — estimation of oxygen in, ii, 302.
 — — haloïds, interaction of alkali haloïds with, TRANS., 540.
 — — metallurgy of, ii, 464.
 — — ores, graphochemistry of, ii, 464.
 — — potassium bromide, ii, 278.
 — — — haloïds, ii, 278, 465, 524.
 — — — iodide, ii, 118, 278; TRANS., 542.
 — — rubidium haloïds, ii, 524.
 — — separation of, from arsenic, ii, 186.
 — — separation of, from silver, ii, 492, 493.
 — — separation of, from tin and antimony, ii, 437.
 — — slags from Raibl, ii, 129.
 — — Stas's determinations of the atomic weight of, ii, 277.
 — — sulphide, ii, 464.
 — — sulphite, ii, 456.
 — — tetracetate, TRANS., 1136.
 — — tetrachloride, ii, 415, 464.
 — — — compounds of, with ammonia and organic bases, ii, 464.
 — — — double salts of, ii, 523.
 — — tetrarpropionate, TRANS., 1136.

- Lead, tin, antimony, and copper, separation of, ii, 95.
 — volumetric estimation of, ii, 302, 599.
 Lead-aluminium-tin alloys, ii, 415.
 Lead-antimony-zinc alloys, ii, 522.
 Lead-silver-aluminium alloys, ii, 416.
 Lead-silver-zinc alloys, ii, 15.
 Lead-tin-zinc alloys, ii, 15.
 Lead-zinc-cadmium alloys, ii, 522.
 Leaf, determination of the starch of the, TRANS., 622.
 — occurrence of diastase in the, TRANS., 632.
 — sugars of the, TRANS., 659.
 Leaves, determination of the diastatic activity of, TRANS., 637.
 — dried, relative diastatic activity of, TRANS., 641, 674.
 — etiolated, amount of ash in, ii, 140.
 — foliage-, chemistry and physiology of, TRANS., 604.
 — periodic variation of the diastase of, TRANS., 644.
 — starch and diastase of, TRANS., 604.
 Lecithin, amount of, in butter, ii, 543.
 Lecithins and phosphorus during development of the hen's egg ii, 289.
 Lecture experiment, preparation of azo-imide, ii, 372.
 — production of hyponitrous acid, ii, 318.
 — with the manocryometer, ii, 566.
 — experiments on explosives, ii, 409.
 Lectures on inorganic chemistry based on the natural system of the elements, ii, 408.
 Leguminosæ, nodule-bearing, utilisation of free atmospheric nitrogen by, ii, 588.
 Leguminous seeds, carbohydrates in, ii, 139.
 Lens, crystalline, proteïds of the, ii, 424.
 Lepidoptera, pigments of, i, 236.
 Lepidopteric acid, i, 236.
 Leptochlorites, composition of, ii, 19.
 Leuchtenbergite, constitution of, ii, 78.
 Leucine, constitution of, i, 195, 309, 501.
 Leucite, basic dyke thought to contain, ii, 539.
 Leucotin, i, 417.
p-Leucotoluidine, TRANS., 1396, 1402.
 Levulan, oxidation of, i, 63.
 Levulinic acid and iodo-formaldehyde, lactone from, i, 628.
 — and its alkyl derivatives, application of the dynamical hypothesis to, i, 499.
 — constitution of, i, 193.
 Levulinic acid, dibromo-, constitution of, i, 689.
 — thermochemistry of, ii, 109.
 Levulose, dextrose, and saccharose, analysis of a mixture of, ii, 99.
 — benzoate, i, 186.
 Licaraldehyde, i, 495.
 Licarene, i, 493.
 — dihydrochloride, i, 493.
 — nitrosochloride, i, 493.
 Licareol, constitution of, i, 496.
 — dextrogyrate, i, 661.
 — tetrabromide, i, 495.
 Licarhodol, i, 545.
 Licaric acid, i, 496.
 Licaronitrile, i, 495.
 Lichens, crystalline acid from, i, 727.
 Light, absorption of, by liquid bromine, ii, 561.
 — action of carbonic anhydride on uranium acetate under the influence of, ii, 484.
 — action of, in inducing the formation of hydrogen peroxide in organic liquids, TRANS., 1109.
 — action of, in preventing putrefaction, TRANS., 1109.
 — action of, on solutions of dimethylaniline, ii, 484.
 — action of, on the isomeric amido-benzoic acids and related compounds, i, 641.
 — cause of the sterilisation of urine by, TRANS., 1119.
 — influence of, on gas exchange, ii, 131.
 — influence of, on metabolic processes, ii, 580.
 — supposed inversion of cane sugar by, i, 547.
 Lignite, vanadiniferous, in the Argentine Republic, ii, 128.
 Lilolidines, i, 521.
 Lilolines, i, 521.
 Lime, action of high temperatures on, ii, 167.
 — inertness of, TRANS., 821.
 Lime-tree honey, i, 618.
 Linalol, action of acetic anhydride on, i, 544.
 Linoleic acid, presence of, in some animal fats, i, 392.
 Linseed cake, adulteration of, ii, 38, 39.
 — analysis of, ii, 39, 40.
 — and meal, manufacture and composition of, ii, 38, 39.
 — oil varnish, testing of, ii, 56, 148.
 — supposed saponification of, by Dutch white lead, PROC., 1893, 122.
 — proteïds of, ii, 292.
 Liquid mass, study of chemical reactions

- in, by means of the index of refraction, ii, 201.
- Liquids, determination of the specific gravity of, ii, 264.
- determination of the thermal expansion of, TRANS., 262.
- extraction apparatus for, ii, 567.
- form of the isothermals for, ii, 152.
- influence of temperature on the rotatory power of, ii, 255, 354.
- laws of the expansion of, ii, 152.
- molecular complexity of, TRANS., 1089.
- relation between the surface tensions and chemical constitution of, ii, 8.
- stirrer for, ii, 452.
- Lithium borates, ii, 460.
- copper chloride, ii, 119.
- flame-spectrum of, ii, 402.
- glycerate, active and inactive, TRANS., 301.
- hydroxide, hydrates of, TRANS., 899.
- infra-red emission spectrum of, ii, 58.
- iodotetrachloride, ii, 68.
- iridochloride, ii, 380.
- nitrate, magnetic rotation of solutions of, TRANS., 67.
- presence of in tomatoes, chick-peas, and *Iris germanica*, ii, 225—227.
- Litmus, sensitive, ii, 294.
- Liver, formation of sugar in the, ii, 25.
- influence of fever on the glycogen of, ii, 541.
- Liver-cells, proteïds of, ii, 133.
- Lupanine, i, 379.
- Lupeose, inversion of, i, 249.
- Lupins, assimilation of nitrogen by, ii, 33.
- Lupinus albus*, alkaloïds from the seeds of, i, 379.
- deliquescent alkaloïd from, i, 739.
- 2:6-Lutidinechloral, i, 527.
- ψ-Lutidostyryl, bromo-, i, 555.
- Lymph, diastatic ferment in the serum of, ii, 333.
- secretion of, ii, 219.

M.

- Madder colouring matters, TRANS., 969.
- Magdala-red, constitution of, i, 721.
- Magenta, constitution of, i, 711.
- Magnesium alkali sulphates, crystallography of, TRANS., 344.
- amalgam, action of, on ethylic iodide, i, 622.

- Magnesium ammonium arsenate, action of heat on, ii, 274.
- calcium, carbonic and sulphuric acids, distribution of acids and bases in a solution containing, TRANS., 696.
- chloride, separation of, from potassium and sodium chlorides, ii, 46.
- decomposition of aqueous vapour by, ii, 168.
- diethide, i, 622.
- dihydrogen phosphate, ii, 277.
- diphenyl, i, 622; PROC., 1893, 81, 111.
- distribution of, in nature, ii, 373.
- glycerate, active and inactive, TRANS., 306.
- hydrogen phosphate, ii, 277.
- nitrate, action of silver oxide on, ii, 12.
- nitride, ii, 209.
- oxide, action of a high temperature on, ii, 167.
- — fusion and volatilisation of, ii, 508.
- phosphate, ii, 168.
- pyrophosphate, action of the electrical arc on, ii, 508.
- separation of, from zinc, ii, 344.
- sulphites, ii, 456.
- use of, for precipitating metals in analysis, ii, 521.
- Magnetic rotation of ethylenic oxide, TRANS., 488.
- — of liquids and salt solutions, ii, 442.
- — of mixed solutions of nitric acid and lithium nitrate, TRANS., 73.
- — of mixed solutions of sulphuric acid and sodium sulphate, TRANS., 69.
- — of nitric acid and its aqueous solutions, TRANS., 57, 65.
- — of solutions of lithium nitrate, TRANS., 67.
- — of solutions of sodium sulphate, TRANS., 64.
- — of sulphuric acid and its aqueous solutions, TRANS., 57, 59.
- rotations of sulphuric acid solutions, TRANS., 99.
- Magnetising iron, electrochemical effects on, ii, 404.
- Maize, losses in ensiling and field curing, ii, 141.
- silage, and field and fodder maize, relative value of, for milk and butter production, ii, 141.
- Maleamic acid, amido-, salts of, i, 632.
- Maleamide, amido-, i, 632.
- Maleic acid and fumaric acid, isomerism of, i, 193.

- Maleic acid, chloro-, i, 318.
 ——— sp. gr. of, i, 11.
 ——— anhydride, heat of hydration of, ii, 108.
Malgedium alpinum, analysis of, ii, 593.
 Malic acid, combination of, with aromatic amines, i, 274.
 ——— derivatives of, i, 500.
 ——— homologues of, i, 146.
 Malic-derivatives, stereochemistry of, i, 457.
 Malonic acid, action of diazobenzene on, i, 82.
 ——— action of iodic acid on, i, 306.
 ——— action of isovaleraldehyde on, TRANS., 1334.
 ——— ureides, thermochemistry of, ii, 360.
 Maltodextrin, nature of, i, 127.
 Maltose, benzoate of, i, 187.
 ——— physiological conversion of, into dextrose, ii, 23.
 Maltosecarboxylic acid, i, 149.
 Mandelic acid, parabromo-, i, 160.
 Manganates, action of sulphur and water on, ii, 205.
 Manganese borate, constitution of, TRANS., 131.
 ——— preparation of, TRANS., 129, 133.
 ——— electrolytic estimation of, ii, 94.
 ——— estimation of, by oxydimetric methods, ii, 497.
 ——— estimation of, in iron, ii, 304.
 ——— estimation of, in minerals, ii, 498.
 ——— estimation of, in ores, ii, 438.
 ——— oxides, estimation of, by means of hydrogen peroxide, ii, 497.
 ——— peroxide, action of a high temperature on, ii, 167.
 ——— preparation of, ii, 281.
 ——— separation of, from nickel, cobalt, and zinc, TRANS., 1082.
 ——— sulphide, ii, 527.
 ——— sulphites, ii, 277, 456.
 ——— volatility of, at high temperatures, ii, 377.
 ——— volatilisation of, in the electric arc, ii, 508.
 ——— zinc, calcium, iron, and aluminium, separation of, ii, 600.
 Manganous acid, basicity and functions of, ii, 416.
 Manganous alkali sulphates, crystallography of, TRANS., 373.
 ——— sulphate, hydrates of, ii, 417.
 Mannitol benzoate, i, 187.
 ——— fermentation of, with a lævolactic ferment, TRANS., 1274.
 ——— specific heat of, ii, 258.
 ——— supposed secondary hexyl alcohol from, i, 246.
 i-Mannoheptitol, i, 148.
 l-Mannoheptitol, i, 148.
 d-Mannoheptonic acid, derivatives of, i, 148.
 i-Mannoheptonic acid, i, 147.
 ——— hydrazide, i, 147.
 l-Mannoheptonic acid, i, 147.
 ——— hydrazide, i, 147.
 ——— lactone, i, 147.
 i-Mannoheptose and its hydrazone and osazone, i, 148.
 l-Mannoheptose and its hydrazone and osazone, i, 148.
 d-Mannose, physiological action of, ii, 585.
 Manocryometer, experiments with, ii, 563.
 ——— lecture experiment with, ii, 566.
 Manure, fermentation of, ii, 182.
 Manures, influence of the distribution of, in the soil on their utilisation, ii, 141.
 ——— loss of nitrogen in, ii, 181, 228.
 ——— nitrogenous, estimation of ammonium thiocyanate in, ii, 347.
 ——— phosphatic and nitrogenous, analysis of, ii, 389.
 Manuring potatoes, ii, 593.
 Marble, statuary, from Rutland, Vermont, ii, 286.
 Margarin, discrimination of butter from, ii, 603.
 Mass, conservation of, in chemical changes, ii, 452.
 Masses, relative, of the atoms of the chemical elements, measurement of the, TRANS., 1.
 Mauveines, constitution of, i, 464.
 Meconinemethyl phenyl ketone, i, 181.
 Mediterranean, Eastern, water and sea-bottom deposits of the, ii, 216.
Melampyrum pratense, analysis of, ii, 593.
 Melanite, artificial production of, ii, 129.
 Melanophlogite, ii, 382.
 Melanostibian, ii, 382.
 Melezitose from lime-tree honey, i, 618.
 Melilite, composition of, ii, 174.
 Melting point, dependence of the solubility of a solid on its, ii, 366.
 ——— points, determination of, under pressure, ii, 563.
 ——— of compounds of similar constitution, TRANS., 465.
 ——— of inorganic substances, determination of, ii, 314.
 Membranes, precipitate, diffusion phenomena with, ii, 203.
 ——— permeability of, ii, 367.
 Memorial Addresses—A. W. HOFMANN, PROC., 1893, 132.

- Memorial Lecture—HERMANN KOPP,
TRANS., 779.
- JEAN-SERVAIS STAS,
TRANS., 1.
- Mentha pulegium*, bases from the oil of,
i, 115.
- Menthol, action of sulphuric acid on,
i, 422.
- American, i, 223.
- tertiary, i, 722.
- Menthylene, i, 422.
- l*-Menthylamine, i, 724.
- r*-Menthylamine, i, 724.
- Menthylamine, tertiary, i, 723.
- Menthylamine - derivatives, rotatory
powers of, i, 725.
- Menthylamines and their derivatives,
i, 105.
- Menthylphenylthiocarbamide, i, 723.
- Mercaptan, molecular weight of, in the
liquid state, TRANS., 1100.
- Mercaptothiazoles, synthesis of, i, 634.
- Mercurammonium salts, i, 304.
- action of potassium iodide or
sodium thiosulphate on, ii, 278.
- Mercuranilido-compounds, i, 322.
- Mercuric chloride, absorption of, from
dilute solutions by cotton, i, 387.
- action of hydrogen sulphide
on, in benzene solution, ii, 72.
- chlorosulphide, ii, 72.
- iodide, solubility of, in diiodometh-
ane, ii, 374.
- oxide, behaviour of, in salt solu-
tions, ii, 450, 566.
- salicylates, i, 642.
- salts, behaviour of, with alumin-
ium, ii, 376.
- Mercurophenylamine salts, i, 322.
- Mercury, abnormal electromotive forces
of, ii, 356.
- action of chlorine on, PROC., 1893,
38.
- action of silicon on, ii, 474.
- detection of, ii, 192, 243, 438.
- detection of, in the organism, ii, 243.
- detection of, in urine, ii, 438.
- electrolytic estimation of, ii, 94.
- electrolytic separation of, from
bismuth, ii, 496.
- electrolytic separation of, from
copper, ii, 305.
- electrolytic separation of, from
lead, ii, 496.
- estimation of, ii, 94, 345, 495.
- estimation of, in dilute solutions
of mercuric chloride, ii, 345.
- fulminate, structure of, i, 494.
- localisation of, in the animal
organism, ii, 217.
- purification of, ii, 322.
- sodium sulphite, ii, 456.
- Mercury, volumetric estimation of,
ii, 495.
- Merotropy, i, 68.
- Mesaconic acid, chloro-, i, 143.
- Mesidine, thionyl-, and its derivatives,
i, 517.
- Mesiten lactone and its derivatives,
action of ammonia on, i, 554.
- Mesitonic acid, preparation of, i, 72.
- Mesitylacetamide, dinitro-, i, 32.
- α -Mesitylamine, i, 32.
- dinitro-, i, 33.
- ω -Mesitylcarbamide, i, 32.
- Mesitylene, i, 32.
- chlorodiiodo-, i, 407.
- critical constants of, ii, 446.
- ω -diamido-, i, 33.
- dichloriiodo-, i, 408.
- diiodo-, i, 407.
- dinitroiiodo-, i, 407.
- formation of, from acetone, i, 498.
- magnetic rotation of, ii, 442.
- nitrodiiodo-, i, 407.
- nitroiiodo-, i, 407.
- triiodo-, i, 407.
- Mesitylenediphtalamic acid, i, 33.
- Mesitylenesulphonic acid, i, 407.
- Mesitylic acid, preparation of, i, 72.
- ω -Mesitylphthalamic acid, i, 32.
- ω -Mesitylphthalimide, i, 32.
- ω -Mesitylthiocarbamide, i, 32.
- Mesolite from Brazil, ii, 422.
- Mesotype-group in the Puy-de-Dôme,
ii, 287.
- Mesoxalic acid, thermochemistry of,
ii, 361.
- dihydrazone, i, 84.
- Metabolic processes, influence of light
on, ii, 580.
- Metabolism during inanition, ii, 477.
- effect of caffeine and coffee distil-
late, on, ii, 329.
- gaseous, influence of acetic acid on,
ii, 21.
- in a child 14 months old, ii, 476.
- in *diabetes mellitus*, ii, 177.
- influence of certain sulphur com-
pounds on, ii, 288.
- influence of chloral hydrate and
amylene hydrate on, ii, 543.
- influence of ligature of the bile
duct on, ii, 329.
- of the dog, influence of dividing the
daily nutriment on, ii, 383.
- Metacamphor, i, 419.
- Metacinnabarite, ii, 215.
- from Idria, ii, 418.
- Metahydroxyuvitic acid, i, 252.
- Metalamine salts, constitution of, ii, 507.
- Metaldehyde and paraldehyde, i, 547.
- transformations of, i, 64.
- molecular weight of, i, 301.

- Metallic oxides, method for reducing, ii, 520.
 Metals, certain, possibility of the vaporisation of, at temperatures below their fusing points, ii, 168.
 — easily volatile, method of observing the spectra of, TRANS., 138.
 — flame spectra of, ii, 402.
 — fusion and volatilisation of, in the electric arc, ii, 507.
 — precipitated by hydrogen sulphide in acid solutions, separation of, ii, 192.
 — volumetric estimation of, ii, 606.
 Metaphosphates, ii, 569.
 Metaphosphoric acid, action of, on organic bases, i, 452.
 — — and pyrophosphoric acid, separation and estimation of, ii, 299.
 Meteoric iron, ii, 20.
 — — from Augustinovka, Russia, ii, 423.
 — — from Cañon Diablo, diamond in, ii, 174.
 — — from Hassi Iekna, Algeria, ii, 79.
 Meteorite from Cañon Diablo, ii, 288.
 — from Central Pennsylvania, ii, 80.
 — from Indian Valley Township, Virginia, ii, 80.
 — from Kenton County, Kentucky, ii, 79.
 — from Mount Joy, Pennsylvania, ii, 216.
 — from the Sierra de la Ternera, Chili, ii, 80.
 — from Wawilowka, ii, 579.
 — of Grossliebenthal, Odessa, ii, 216.
 Meteorites, Turkish, ii, 578.
o-Methamidobenzoic acid, i, 414.
 — nitroso-, i, 414.
 Methane, action of stannic chloride on halogen derivatives of, i, 121.
 — and oxygen, ignition temperature of a mixture of, ii, 258.
 — bromonitro-, formation of, i, 542.
 — dibromodinitro-, i, 689.
 — heat of combustion of, ii, 444.
 — trichloronitro-, melting point of, ii, 357.
 Methanesulphonic chloride, trichloro-, i, 458.
 Methenyldiparatolyltriimidotoluene, TRANS., 1405.
 Methenylpara-*n*-methyltolylenediamine, i, 285.
 Methocarbonyl- β -amidopropionic acid, i, 310, 631.
 1-Methoxy-4-acetamidoquinoline, i, 607.
 Methoxyamidodimethylbenzene [1 : 2 : 4 : 6] and its derivatives, TRANS., 104.
p-Methoxybenzenesulphonamide, i, 639.
p-Methoxybenzoisulphimide, i, 585.
 1-Methoxy-4-benzoylamidoquinoline, i, 607.
 Methoxybenzylidene, i, 703.
 Methoxybenzylidenemesidine, i, 517.
 Methoxycoumaronealdehyde, nitro-, i, 342.
 Methoxycoumaronecarboxylic acid, nitro-, i, 342.
 Methoxydimethylhydroxyquinaldine [1 : 2 : 4 : 4], TRANS., 108.
 Methoxyhydroxydimethylbenzene [1 : 2 : 4 : 6], TRANS., 107.
p-Methoxymetasulphonaminebenzoic acid, i, 585.
 Methoxynaphthalene, 1 : 4-nitro-, i, 39.
 Methoxynitrodimethylbenzene [1 : 2 : 4 : 6], TRANS., 106.
 Methoxynitro-xylene, TRANS., 106.
p-Methoxyorthosulphobenzoic acid, i, 586.
 4-Methoxyphthalazine, i, 347.
 1-Methoxyquinoline, nitro- and dinitro-, i, 607.
 Methoxysuccinamic acid, i, 310, 631.
 Methoxysuccinic acid, resolution of, into its optically active components, TRANS., 217.
p-Methoxytoluenemetasulphonic acid, i, 585.
p-Methoxytolueneorthosulphonic acid, i, 585.
 2-Methoxyxanthone, i, 218.
 3-Methoxyxanthone, i, 218.
 4-Methoxyxanthone, i, 218.
 Methyl dichloropropyl ketone, action of potassium carbonate on, i, 391.
 — ethyl ketone, specific volume and thermal expansion of, TRANS., 283.
 — heptylene ketone, i, 107, 597.
 — isopropyl ketone, TRANS., 1336.
 — propyl ketone, molecular weight of, in the liquid state, TRANS., 1101.
 — — specific volume and thermal expansion of, TRANS., 284.
 Methylacetalyphenylcarbamide, i, 340.
 Methylacetylacetone, action of ammonia on, i, 454.
 Methylacetylurethane, i, 128.
 Methylacridone, i, 650.
 Methylacrylamide, i, 695.
 β -Methyladipic acid, derivatives of, i, 396.
 Methylallantoin, thermochemistry of, ii, 360.
 Methylallylisopropylcarbinol, preparation of, TRANS., 1336.
 3-Methyl-4-allylpyrazolone, i, 429.
 Methylamidobenzenes, relations between constitution and physical constants in the case of, PROC., 1893, 41.

- Methylamidophenylglyoxylic acid,
 ortho-, nitrosamine of, i, 280.
 1 : 2-Methylamidoquinoline, i, 604.
 Methylamidoquinolinecarboxylic acid,
 [1 : 2 : 4], i, 604.
 Methylamidoquinolinesulphonic acid
 [1 : 2 : 4], i, 603.
 Methylamine, freezing points of aqueous
 solutions of, TRANS., 149.
 — hydrate of, TRANS., 148.
 — thionyl-, i, 504.
 Methylamines and ammonia, analysis of
 mixtures of, ii, 104.
 Methylaniline, aniline, and dimethyl-
 aniline, estimation of, i, 23.
 — paranitrothamido-, i, 200.
 Methylanilinephenylsulphone, i, 205.
n-Methylbenzenyltolyleneamidine,
 i, 285.
 2-Methylbenzimidazole-2'-carboxylic
 acid, i, 436.
 2'-Methylbenzimidazole-2-carboxylic
 acid, i, 436.
 Methylbenzoic anilide, preparation of,
 i, 268.
 4' : 2'-Methylbenzylphenometadiazine,
 i, 532.
 Methylbrazilin, i, 426.
 Methylbromolapazine, TRANS., 1382.
 Methylbutenylmethylthionylamine,
 i, 702.
 Methylbutylketoxime, i, 499.
 Methylbutylthiourea, secondary, TRANS.,
 321.
 Methylchavicol, thermochemistry of,
 ii, 154.
 Methylchloramine, i, 497.
 Methylchloronaphtheurhodone, TRANS.,
 1386.
 1 : 4-Methylchlorophthalazine, i, 348.
 Methylcitraconic acid, i, 194.
 Methylconiine, i, 442.
 3' : 4'-Methyleyanisocarbostyryl, i, 228.
 Methylcytisine, i, 120.
 Methyl dibromomethylol, i, 316.
 Methyl dichlorometadiketopentene,
 i, 260, 319.
 1-Methyldihydroisindole, i, 348.
 1'-Methyldihydroisquinoline, i, 608.
n-Methyldihydromethylketole and its
 derivatives, i, 521.
 β -Methyl- $\alpha\alpha'$ -dihydroxypyridine,
 TRANS., 880.
 α_2 -Methyl- $\alpha\gamma$ -diketolilolidine, i, 522.
 Methyl diphenylamine, action of ethylic
 orthoformate on, i, 686.
 Methyl diphenylindole [1' : 2' : 3'],
 i, 520.
 Methyl diphenylpiperazine, i, 80.
n-Methyl diphenyltoluidohydroquinoxal-
 ine, i, 285.
 Methyl dipyrindyls, i, 612.
 Methylene-blue dyes, conversion of
 metamidodialkylorthotoluidines into,
 i, 75, 77.
 Methylene dicatichol, i, 274.
 Methylene dihydroxynaphthoic acid,
 i, 100.
 Methylene di- β -naphthol, i, 100.
 Methylene dinaphthylene oxide, i, 222.
 Methylene diorthonitraniline, i, 389.
p-Methylene hydrobenzamide, i, 713.
p-Methylene hydrobenzoic acid, i, 378.
 Methylene bromide, action of stannic
 chloride on, i, 121.
 — iodide, action of stannic chloride
 on, i, 121.
 Methylene paramethoxycinchoninic acid,
 i, 729.
 Methylene phthalamic acid, i, 389.
 1 : 4-Methylethoxyphthalazine, i, 348.
 Methylene ethylenic chloride, i, 381.
 4' : 2'-Methylene thylphenometadiazine,
 i, 531.
 Methylene thylphenyl trichloropyrazole,
 dichloroplato-, i, 672.
 Methylene thylphenyl trimethylene di-
 amine, i, 177.
 — methylene thyl trimethylene anilthio-
 carbamate, i, 178.
 1 : 3-Methylene thyl phthalazone, i, 347.
 Methylene thyl tetine bromide, i, 633.
 Methylene eugenol, action of nitrous acid
 on, i, 103.
 — nitrosite anhydride, i, 197.
 — thermochemistry of, ii, 154.
 Methyl fisetol, action of phenylhydrazine
 on, i, 413.
 Methyl furfuraldehyde, i, 311.
 Methyl furfuralamide, i, 312.
 Methyl glutaric acid, TRANS., 879.
 Methyl heptylenecarbinol, i, 597.
 Methyl hexyldiphenoxymethane, i, 215.
 Methyl hexylenecarbinol, i, 593.
 Methyl hydrastine oxime anhydride,
 i, 118.
 Methyl hydrastine phenylhydrazine an-
 hydride, i, 118.
 Methyl hydrastimide, nitro-, i, 119.
 Methyl hydroxyhydrolapeurhodone,
 TRANS., 1384.
 Methyl hygrine oxime hydriodide,
 i, 446.
 Methyl acetate, heat of vaporisation
 of, ii, 446.
 — — vapour pressure, molecular
 volume, and critical constants of,
 TRANS., 1207.
 — acetylenedicarboxylate, action of
 diazobenzeneimide on, i, 570.
 — — action of ethylic diazoacetate
 on, i, 439.
 — alcohol as a solvent, i, 244.
 — alcohol, depression of the freez-

- ing point of acetic acid by, TRANS., 1023.
- Methylic alcohol, depression of the freezing point of benzene by, TRANS., 1019.
- depression of the freezing point of water by, TRANS., 1015.
- detection of impurities in, ii, 196.
- heat of vaporisation of, ii, 446.
- magnetic rotation of, ii, 442.
- molecular weight of, in the liquid state, TRANS., 1102.
- amidomethyleneglutaconate, i, 402.
- anilidomethyleneglutaconate, i, 402.
- 4-azobenzenepyrrolone-3-carboxylate, i, 730.
- 4-benzalpyrazolone-3-carboxylate, i, 730.
- benzenecyanacetate, i, 466.
- benzenesulphinic acid, i, 344.
- benzoylbenzenecyanacetate, i, 466.
- bisdihydrosantinate, i, 425.
- brassylate, i, 551.
- *p*-bromobenzenesulphinic acid, i, 344.
- butyrate, vapour pressure, molecular volume, and critical constants of, TRANS., 1229.
- carboxydehydracetate, i, 399.
- chloride and carbonic anhydride, measurement of Van der Waals' surface for mixtures of, ii, 260.
- β -chloropropionate, i, 688.
- diacetylglycerate, active, TRANS., 1421.
- inactive, TRANS., 1420.
- dibromogallate, i, 343.
- diglycolate, i, 191.
- diiodofumarate, i, 397.
- 2:3-diphenylpiazinecarboxylate, TRANS., 1307.
- ethylenedi- β -amidocrotonate, TRANS., 1311.
- formate, molecular weight of, in the liquid state, TRANS., 1100.
- vapour pressure, molecular volume, and critical constant of, TRANS., 1195.
- formazylcarboxylate, i, 82.
- gallate, i, 343.
- glycerate, active and inactive, TRANS., 513.
- hydrindenecarboxylate, i, 717.
- hydrogen camphorate, ortho-, i, 278.
- allo-, i, 278.
- *p*-toluidomethyleneglutaconate, i, 403.
- hydroxymethyleneglutaconate, i, 402.
- iodide, action of stannic chloride on, i, 121.
- Methylic isobutyrate, vapour pressure, molecular volume, and critical constants of, TRANS., 1234.
- 4-isonitrosopyrazolone-3-carboxylate, i, 730.
- mercaptan, production of, by a bacterium in urine, ii, 335.
- mesitencarbamate, i, 555.
- mesoxalate hydrazone, i, 82.
- methocarbonyl- β -amidopropionate, i, 631.
- methoxybenzylsodiummalonate, i, 583.
- methoxymethyleneglutaconate, i, 401.
- methoxypiperonylsodiummalonate, i, 583.
- methylbenzenecyanacetate, i, 466.
- α -naphthalenesulphinic acid, i, 343.
- β -naphthalenesulphinic acid, i, 343.
- orthoethylic pyrotartrate, i, 252, 307.
- α -phenyl- β -bromocinnamate, i, 342.
- propionate, vapour pressure, molecular volume, and critical constants of, TRANS., 1219.
- pyrazole-3:5-dicarboxylate, i, 431.
- pyrazole-3:4:5-tricarboxylate, i, 432.
- pyrazoline-3:5-dicarboxylate, i, 431.
- pyrazoline-3:4:5-tricarboxylate, i, 431.
- pyrazolonecarboxylate, i, 730.
- pyrotartrate, ortho-, i, 252, 307.
- succino- β -ureidopropionate, i, 632.
- *o*-sulphaminebenzoate, i, 715.
- sulphide, specific volume and thermal expansion of, TRANS., 287.
- tetrahydroparatoluic acid, i, 713.
- thiodiglycolate, i, 191.
- thionylmetamidobenzoate, i, 517.
- *p*-toluenesulphinic acid, i, 344.
- *p*-toluidomethyleneglutaconate, i, 402.
- trichloracetate, trichloro-, i, 188.
- β -ureidopropionate, i, 632.
- Methylimidazole, i, 734.
- Methylimidazolyl- μ -mercaptan, i, 734.
- n*-Methylindazole, i, 280.
- p*-Methylindazole, i, 280.
- p*-Methylindazolecarboxylic acid, i, 280.
- Methylindoxazen, nitro-, attempts to prepare, TRANS., 1353.
- Methylinositol, i, 295.
- Methylisoamylketoxime, i, 499.
- Methylisoamylthiourea, TRANS., 323.
- Methylisobutylthiourea, TRANS., 320.
- 3'-Methylisocarbostyryl, i, 228.
- 3'-Methylisocoumarin, i, 228.

- Methylisoeugenol, thermochemistry of, ii, 154.
- Methylisindole, i, 348.
- Methylisonitrosocamphor, i, 660.
- m*-Methylisopropylbenzene, i, 597.
- Methylisopropylidihydrobenzene, i, 258.
- β -Methylisopropyl- β -lactic acid, preparation of, TRANS., 1337.
- Methylisopropylphenanthramethylpiazine, TRANS., 1291.
- 1:4-dihydride, TRANS., 1291.
- Methylisopropylphenanthrapiazine, TRANS., 1288.
- 1:4-dihydride, TRANS., 1288.
- 4':2'-Methylisopropylphenometadiazine, i, 531.
- 3'-Methylisoquinoline, i, 228.
- 1'-chloro-, i, 228.
- 1'-Methylisoquinolone, i, 279.
- Methylisoxazonimide, i, 315.
- Methylitaconic acid, i, 194.
- 3-Methyl- Δ_2 -ketohexenylene, i, 394.
- 3-Methyl- Δ_2 -ketohexenylenecarboxylic acids, i, 393.
- Methylketole, bromine derivative of, i, 169.
- β -Methylketopentamethylene, i, 130.
- Methyllapazine, TRANS., 1381.
- Methylapeurhodone, TRANS., 1383.
- Methylmalic acid, i, 146.
- Methylmercaptothiazole, i, 634.
- Methylmesaconic acid, i, 194.
- Methylnaphthalenes, i, 171.
- Methyl-*a*-naphtheurhodol, TRANS., 1385.
- n*-Methylnaphthophenazonium hydroxide, i, 282.
- iodide, i, 282.
- 1'-Methylnitrosoquinolone, i, 279.
- Methylorthophenylenediamine, oxidation of, i, 199, 266.
- Methylorthotoluidine, metanitro-, i, 76.
- β -Methylorthotoloxazoline, i, 533.
- β -Methylorthotolylthiazoline, i, 533.
- Methyl- $\alpha\beta$ -oxynaphthindone, i, 338.
- Methyloxythiazole, preparation and properties of, i, 228.
- 2:3-Methylparabromophenyldihydroquinazoline, i, 440.
- Methylparahydroxybenzoylbenzoic acid, i, 719.
- 2:3-Methylparatolyldihydroquinazoline, i, 440.
- β -Methylparatoloxazoline, i, 533.
- β -Methylparatolylthiazoline, i, 533.
- β -Methylpentamethylenol, i, 130, 396.
- β -Methylpentamethylenylamine, i, 130.
- β -Methylpentamethylenylene, i, 396.
- μ -Methylpenthiazoline, i, 427.
- Methylphenanthridone, i, 658, 722.
- Methylphenazonecarboxylic acid, i, 734.
- Methylphenylacrylamide, i, 696.
- Methylphenylauramine, salts of, i, 473.
- 2:3-Methylphenyldihydroquinazoline, i, 439.
- 4':2'-Methylphenylethenylphenometadiazine, i, 532.
- Methylphenylketoxime, ethyl derivative of, i, 499.
- Methylphenylmercurammonium hydroxide and salts, i, 24.
- 4':2'-Methylphenylphenometadiazine, i, 531.
- B*₄-2-Methylphenylrosinduline, i, 335.
- Methyl- μ -phenylthiazoline, i, 534.
- 1-Methylphthalazone, i, 347.
- 3-Methylphthalazone, i, 346.
- 1-Methylphthalimidine, i, 347.
- 1-Methylpipercolylalkine, i, 426.
- Methylpiperidine platinochloride, i, 602.
- Methylpropylbenzenes, i, 562.
- 4':2'-Methylpropylphenometadiazine, i, 531.
- Methylpropylphenylacetic acid, i, 465.
- Methylpurpuroxanthin, synthesis of, TRANS., 1142.
- 2:5-Methylpyrazinecarboxylic acid, i, 487.
- Methylpyrazole, i, 179.
- 3:5-Methylpyrazolecarboxylic acid, i, 179.
- Methylpyridinedicarboxylic acid, i, 175.
- 1-Methyl-2-pyridone, i, 279.
- Methylpyromucamide, i, 312.
- Methylpyromucic acid, i, 312.
- sulpho-, i, 312.
- acids, bromo-, i, 312.
- Methylpyrrolines, constitution of, i, 226.
- 1'-Methyl-2'-quinolone, i, 279.
- Methylresorcinol, condensation of, with nitrobenzaldehydes, i, 216.
- Methylsalicylic acid, detection of free salicylic acid in, ii, 503.
- u*-Methylselenazoline, i, 30.
- Methylsulphoneacetic acid, i, 459.
- Methylsulphurous chloride, trichloro-, preparation of, ii, 571.
- Methyltetrahydroisoquinoline methiodide, i, 227.
- Methyltetrazylpyrazolone, i, 442.
- μ -Methylthiazoline, i, 427.
- Methylthiohydantoin, TRANS., 819.
- Methyltolylenediamine [1:3:4], i, 285.
- Methyltrimethenyldicarboxylic acid, asymmetrical, i, 404.
- — symmetrical, i, 404.
- — dibromo-, i, 404.
- 3-Methyl-4-trimethylenepyrazolone, i, 429.
- Methyltyrosine, i, 182.
- 1-Methylvinylpiperidine, i, 426.

- 4-Methylxanthone, i, 217.
 Mica, constitution of, ii, 78.
 Mica-peridotite from Kentucky, ii, 79.
 Microbes, absorption of atmospheric nitrogen by, ii, 83.
 — assimilation of atmospheric nitrogen by, ii, 482.
 Micro-organisms, nitrogen - fixing, ii, 429.
 Milk, abnormal, ii, 428.
 — digestibility of, ii, 580.
 — estimation of fat in, ii, 55, 101, 251, 252, 308, 396, 559, 601.
 — estimation of fat in, by Babeock's method, ii, 251.
 — estimation of fat in, by Leffmann and Beam's method, ii, 308.
 — estimation of fat in, with Demichel's lactobutyrometer, ii, 55.
 — estimation of lactic acid in, ii, 250.
 — estimation of total solids in, ii, 252, 559.
 — fat, influence of sugar on the constitution of, ii, 27.
 — goat's, and its detection in admixture with cow's milk, ii, 396.
 — of different breeds of cows, ii, 220.
 — production, relative value of maize silage, and field and fodder maize for, ii, 141.
 — the phosphates of, ii, 582.
 — sterilised, behaviour of, towards digestive fluids, ii, 217.
 — transmission of alcohol to, ii, 219.
 — use of metaphosphoric acid to remove proteids in estimating sugar in, ii, 248.
 Milks, identification and estimation of the lactoses in different, ii, 502.
 Milk-sugar, benzoate of, i, 186.
 Mineral from Boléo, Mexico, ii, 417.
 Mineral oil, detection and estimation of neutral fats in, ii, 604.
 Minerals, synthesis of, ii, 422.
 — use of thallium silver nitrate, for separating, ii, 294.
 Minervite, ii, 577.
 — formation of, ii, 536.
 Molasses, influence of raffinose and of calcium salts on the formation of, i, 683.
 Molecular complexity of liquids, TRANS., 1089.
 — dissymmetry, ii, 204.
 — refraction and dispersion, ii, 254.
 — refractive power of organic compounds for infinite wave-length, ii, 57.
 — volume of sulphuric acid in solution, TRANS., 102.
 — volumes of certain ethereal salts, TRANS., 1191, 1246, 1247.
 Molecular volumes of dissolved alkali salts, ii, 264.
 — weight, determination of, at the critical point, ii, 204.
 — — determination of, from the rate of evaporation, ii, 261.
 — — of a dissolved substance and the specific gravity of its solution, relation between, ii, 7.
 — — of hydrogen peroxide, ii, 163.
 — weights, determination of, by Beckmann's method, ii, 511.
 Mollusca, δ -achroglobin from the blood of, i, 615.
 Molybdates, combination of, with selenious acid, ii, 531.
 — combination of, with sulphurous acid, ii, 530.
 Molybdenum, action of carbonyl chloride and of sulphur chloride on, ii, 574.
 — action of, on solutions of silver, gold, &c., ii, 170.
 — oxide, new, ii, 472.
 — oxyfluoride, new, ii, 472.
 — preparation of, in the electric furnace, ii, 471.
 Molybdenyl chloride, action of gaseous ammonia on, ii, 529.
 Molybdic acid, action of hydrogen haloids on, ii, 471.
 — anhydride, compounds of, with alkali oxalates, i, 457.
 Molybdoarsenates, ii, 282.
 Molybdoarsenic acid, ii, 282.
 Molybdoperiodic acid, salts of, ii, 123.
 Molybdoselenious acid, ii, 531.
 Monoketopiperazines, i, 53.
 Mordants, theory of the formation of coloured compounds with, i, 510.
 Mordenite, constitution of, ii, 77.
 Morinda root, colouring principles of, TRANS., 1184.
 Morphine, constitution of, i, 536.
 — effect of, on the work of the kidney, ii, 542.
 — resistance of goats to the action of, ii, 335.
 — titration of, ii, 607.
Mosula japonica, thymol in the ethereal oil of, ii, 181.
 Motochemistry or stereochemistry?, ii, 513.
 Mucic acid, preparation of, from gum arabic, i, 628.
 Mucin, ii, 330.
 — in bone, ii, 134.
 Mucin-granules of *Myxine*, ii, 429.
 Munjustin from *Rubia sikkimensis*, TRANS., 1159.
 Murexide, thermochemistry of, ii, 361.

- Muscarine**, i, 297.
 — action of aniline on, i, 45.
Muscle, acid reaction of, ii, 176.
 — calculus in, ii, 334.
 — sugar in, ii, 383.
 — voluntary, action of sodium oxalate on, ii, 480.
Muscular tissue, action of nitrites on, ii, 384.
 — work, alkalinity of the blood during, ii, 218.
 — — fatiguing, action of, on respiratory interchange, ii, 21.
Myricylic acetate, i, 683.
 — alcohol, i, 683.
 — benzoate, i, 683.
 — cerotate, i, 683.
 — hydrogen phthalate, i, 683.
 — laurate, i, 683.
 — oxalate, i, 683.
 — palmitate, i, 683.
Myristone, preparation of, TRANS., 458.
Myristoneoxime, TRANS., 458.
Myxine, mucin granules of, ii, 429.

N.

- Napelline**, TRANS., 443.
Naphthaldehydic acid and its derivatives, i, 657.
Naphthalene, action of ammonium hydrogen sulphate on, i, 411.
 — action of nitric peroxide on, TRANS., 1393.
 — action of nitro-compounds on, TRANS., 1392.
 — constitution of, i, 603.
 — cryoscopic behaviour of benzene solutions of, ii, 110.
 — depression of the freezing point of benzene by, TRANS., 1022.
 — 1 : 3-, 1 : 2'-, and 1 : 3'-dichloro-, i, 651.
 — di-derivatives of, nomenclature of, i, 651.
 — nitration of, at low temperatures, i, 460.
 — ortho-, para-, and peri-disulphonic derivatives of, PROC., 1893, 166.
 — orthodibromo-, TRANS., 1054.
 — peri-derivatives of, TRANS., 1054.
 — peridibromo-, TRANS., 1059.
 — perinitrobromo-, TRANS., 1057.
 — sulphonic derivatives of, i, 276.
 — synthetical tri-derivatives of, i, 653.
Naphthalene-derivatives, isomeric, separation of, i, 651.
 — physiological action of, ii, 544.
Naphthalene-derivatives, production of, from dehydracetic acid, TRANS., 329.
 1 : 2-Naphthalenedisulphonic acid, PROC., 1893, 168.
 1 : 4-Naphthalenedisulphonic acid, PROC., 1893, 168.
 1 : 1'-Naphthalenedisulphonic acid, PROC., 1893, 168.
 α -Naphthalenesulphinic acid, perinitro-, i, 652.
 α -Naphthalenesulphonic acid, dinitro-, i, 652.
 — — 1'-nitro-, i, 651.
 — — 4'-nitro-, i, 652.
 — — electrolytic reduction of, i, 567.
Naphthalenesulphonic acids, substituted, compounds of, with organic bases, i, 653.
 α -Naphthalenesulphonic acids, α -nitro-, i, 651.
 α -Naphthalenesulphonic chloride, 1'-nitro-, i, 651.
 2 : 2' : 3'-Naphthalenetrisulphonic acid, PROC., 1893, 168.
Naphthalic acid, oxidation of, i, 593.
 1 : 1'-Naphthalic acid and its derivatives, i, 477.
 — — imide of, and its derivatives, i, 477.
Naphthalic anhydride, i, 477.
Naphthalidonaphthaquinonenaphthalide, i, 339.
Naphthaphenazine oxide, i, 356.
 β -Naphthaquinone, reduction of, with hydriodic acid, TRANS., 774.
 $\alpha\beta$ -Naphthazine, asymmetrical and symmetrical, i, 283.
 — oxy-, i, 339.
 $\beta\beta$ -Naphthazine and its derivatives, i, 283.
Naphthencarboxylic acids, nature of, i, 209.
Naphthenes, action of bromine on, in presence of aluminium bromide, i, 13.
 β -Naphtheurhodole, i, 356.
Naphthidine, preparation of, i, 421.
 $\alpha\beta$ -Naphthinduline, i, 337.
Naphthindulines, i, 334.
Naphthionic acid, behaviour of the sodium and potassium salts of, at high temperatures, i, 655.
Naphthoic acid, β -chloro-, i, 355.
 β -Naphthoic acid, amidodisulpho-, i, 475.
 α -Naphthofluoran, i, 275.
 β -Naphthofluoran, i, 275.
 α -Naphthol, 1' : 4'-dichloro-, i, 653.
 — 2' : 4'-dichloro-, i, 653.
 — periromo-, TRANS., 1058.
 — products of the direct sulphonation of, i, 221.

- β -Naphthol, 1-amido-, acetyl derivatives of, i, 171.
 — α -amido-, action of nitrous acid on, i, 171; *Proc.*, 1892, 218.
 — compound of, with aluminium chloride, i, 508.
 β -Naphtholcarboxylic acid (m. p. 216°), derivatives of, i, 221.
 α -Naphtholdisulphonic acids, amido-, i, 478.
 α -Naphtholazoparatoluic acid, i, 202.
 β -Naphtholazoparatoluic acid, i, 202.
 β -Naphtholazoparatoluonitrile, i, 202.
 Naphthol-blue, action of aniline on, i, 45.
 Naphthols, condensation of chloral hydrate with, i, 173.
 — condensation of, with formaldehyde, i, 172.
 — dichloro-, from 3 : 4 : 1-dichlorophenylisocrotonic acid, i, 653.
 α -Naphtholsulphonic acids, i, 221.
 — — amido-, i, 478.
 $\alpha\beta$ -Naphthophenazine, i, 284.
 β -Naphthophosphoric acid, i, 355.
 — chloride, i, 355.
 α -Naphthyl ethyl ether, action of phenylthiocarbimide on, i, 154.
 α -Naphthylacetylene, derivatives of, i, 421.
 β -Naphthylacetylene, derivatives of, i, 421.
 α -Naphthylamine, bromo-, i, 706.
 — 1' : 4'-dichloro-, i, 653.
 — 2' : 4'-dichloro-, i, 653.
 — 2 : 4-dinitro-, preparation of, from its acetyl and valeryl derivatives, *Proc.*, 1893, 7.
 — peribromo-, *Trans.*, 1057.
 — perinitro-, preparation of, *Trans.*, 1055.
 — sulphonation of, i, 653.
 β -Naphthylamine, dibromo-, i, 706.
 α -Naphthylaminedisulphonic acid III, Dahl's, i, 654.
 ξ -Naphthylaminedisulphonic acid, i, 655.
 Naphthylamines, thionyl-, and their derivatives, i, 518.
 α -Naphthylamine-3'-sulphonic acid, i, 654.
 ν -Naphthylaminesulphonic acid, i, 655.
 Naphthylaminesulphonic acids, affinity coefficients of, ii, 450.
 — — physical properties of, i, 655.
 β -Naphthylazobromonitroethane, i, 656.
 Naphthylazo-compounds, mixed, i, 655.
 α -Naphthylazonitroethane, i, 656.
 β -Naphthylazonitroethane, i, 655.
 β -Naphthylazonitrosnitroethane, i, 656.
 β -Naphthyl diazoimide, i, 706.
 α -Naphthyl- $\alpha\gamma$ -diketo- $\beta\delta$ -dimethylpiperazine, i, 52.
 β -Naphthyl dimethylpyrimidine, i, 735.
 α -Naphthylethylsulphone, i, 276.
 β -Naphthylethylsulphone, i, 276.
 β -Naphthylhydrazine, bromination of, i, 705.
 Naphthyl acetylsalicylates, i, 514.
 — dibromosalicylates, i, 514.
 — ethers, substitution products of, i, 274.
 — nitrosalicylate, i, 514.
 — salicylate phenylcarbamates, i, 514.
 α -Naphthyl titanate, i, 257.
 β -Naphthyl benzoate, compound of, with aluminium chloride, i, 508.
 — phthalate, i, 275.
 α -Naphthylindole, i, 169.
 α -Naphthylketopiperazine, i, 54.
 β -Naphthylmetaphenylenediamine, i, 420.
 α -Naphthylmethylsulphone, i, 276.
 β -Naphthylmethylsulphone, i, 276.
 α -Naphthylpropionic acid, i, 421.
 Naphthyl-red, i, 721.
 Naphthyl-violet, i, 337, 338.
 Nectarines, Californian, analyses of, ii, 591.
 Nerve, medulla of, chemical constituents of, i, 234.
 Nerves, chemical stimulation of, ii, 221.
 Nervous tissues, proteids of, ii, 478.
 Niaouli, essential oil of, i, 523, 727.
 Niche, i, 57.
 — nitroso-, i, 737.
 — salts of, i, 737.
 Nickel, analysis of, ii, 393.
 — and cobalt, separation of, by means of nitrosnaphthol, ii, 500.
 — and iron, supposed new sulphides of, ii, 535.
 — atomic weight of, ii, 212, 469, 574.
 — electrolytic estimation of, ii, 94.
 — electrolytic separation of bismuth from, ii, 496, 497.
 — electrolytic separation of copper from, 306, 496.
 — elementary nature of, ii, 212, 469.
 — gas-volumetric estimation of, ii, 393.
 — oxide, action of a high temperature on, ii, 167.
 — separation of manganese from, *Trans.*, 1082.
 — sulphide, oxidation of, ii, 528.
 — sulphite, basic, ii, 456.
 — tetracarbonyl, molecular weight of, in the liquid state, *Trans.*, 1099.
 — — spectra of the flame of, ii, 401.
 Nickeliferous iron pyrites from Müsen, ii, 18.
 Nickel-ore, platiniferous, from Canada, ii, 286.

- Nickelous alkali sulphates, crystallography of, *TRANS.*, 379.
- Nicotine, i, 443.
- acetate, cryoscopic behaviour of, i, 667.
- and conine, discrimination and separation of, ii, 607.
- condensation of, with acetaldehyde, i, 737.
- constitution of, i, 286, 375, 489, 675, 736.
- salts, decomposition of, and action of alcohol on, i, 445.
- Nicotinic acid, 2-amido-, i, 727.
- 3-bromo-, i, 484.
- 4'-bromo-, i, 484.
- hydrobromide, i, 484.
- 3 : 2-nitramido-, i, 727.
- Nitrates, action of sulphurous anhydride on, ii, 115.
- and chlorates, estimation of, in one operation, ii, 596.
- and nitrates, estimation of, in one operation, ii, 596.
- and nitrites, estimation of, in one operation, ii, 596.
- are, indispensable for the growth of plants? ii, 385.
- estimation of, by ferrous salts, ii, 595.
- estimation of, by Schmitt's method, ii, 551.
- estimation of nitrogen in, ii, 42, 87, 184, 343, 389, 434, 551.
- estimation of nitrogen in, by Kjeldahl's method, ii, 87.
- in rain, ii, 548.
- iodometric estimation of, ii, 42, 551.
- modified Gunning-Kjeldahl method, for use in presence of, ii, 145.
- organic, estimation of nitrogen in, ii, 184.
- recently formed, greater assimilability of the nitrogen of, ii, 548.
- Nitre, direct estimation of nitrogen in, ii, 343.
- Nitric acid and its aqueous solutions, magnetic rotation of, *TRANS.*, 57, 65.
- and nitric oxide, reaction between, ii, 413.
- decomposition of, by heat, ii, 423.
- estimation of, by its specific gravity, ii, 66.
- estimation of, by means of cinchonamine salts, ii, 297.
- estimation of nitrogen in, ii, 389.
- freezing points of aqueous solutions of, *TRANS.*, 440.
- influence of nitric peroxide on the sp. gr. of, ii, 66.
- Nitric acid, isolation of two predicted hydrates of, *TRANS.*, 436.
- presence of nitrous acid in, ii, 206.
- products of the action of, on tin, *TRANS.*, 846.
- reduction of, by copper, ii, 272.
- reduction of, by ferrous salts, ii, 595.
- Nitric oxide and nitric acid, reaction between, ii, 413.
- behaviour of, at high temperatures, ii, 66.
- density of, ii, 272.
- preparation of, ii, 298.
- Nitrification, ii, 544.
- in soil, ii, 486.
- Nitriles, aromatic, hydrolysis of, i, 541.
- dimolecular, reactions of, i, 314.
- Nitrites, action of, on muscular tissue, ii, 384.
- and hydroxylamine salts, velocity of reaction between, ii, 160.
- estimation of, ii, 87, 344, 346.
- estimation of, by Schäffer's reaction, ii, 344.
- in potable water, estimation of, ii, 346.
- Nitro-compounds, action of aluminium chloride with, i, 161.
- action of hydrazine hydrate on, i, 701.
- aromatic, electrolytic reduction of, i, 566.
- combinations of, with hydrocarbons, *TRANS.*, 1388.
- estimation of nitrogen in, by Kjeldahl's method, ii, 87.
- explosive, analysis of, ii, 196.
- heats of combustion of, ii, 59.
- structure of, i, 636.
- Nitro-derivatives, formation of, at low temperatures, i, 460.
- Nitrogen, action of, on charcoal, ii, 571.
- and carbon, compounds containing double linking between, i, 409.
- simultaneous estimation of, in organic compounds, ii, 501.
- atmospheric, absorption of, by microbes, ii, 83, 429, 482.
- assimilation of, by plants, ii, 33, 84, 138, 336, 590.
- atom, the asymmetrical, i, 442.
- atomic refraction of, ii, 254.
- attempts to condense, ii, 270.
- chloride, decomposition of, by water, i, 388.
- combined, in rain, ii, 548.
- compounds, stereoisomerism of, *TRANS.*, 1069.
- density of, ii, 453, 515.

Nitrogen, diffusion of, in water, ii, 62.
 — direct estimation of, in saltpetre, ii, 343.
 — effect of an electric discharge on, ii, 271.
 — effect of sterilisation on the fixation of, in soil, ii, 291.
 — estimation of, by Kjeldahl's method, ii, 43, 87, 88, 144, 145, 551.
 — estimation of, by Stock's process, ii, 297.
 — estimation of, by the Gunning-Kjeldahl method and a modified form thereof, ii, 235.
 — estimation of, in coal gas, ii, 296.
 — estimation of, in nitrates, ii, 42, 87, 184, 434, 389.
 — estimation of, in nitrates and nitro-compounds by Kjeldahl's method, ii, 87.
 — estimation of, in nitric acid, ii, 389.
 — estimation of, in nitrocellulose, ii, 184.
 — estimation of, in organic nitrates, ii, 184.
 — estimation of, in organic substances by Dumas' method, ii, 297.
 — estimation of, in sodium nitrate, ii, 87.
 — estimation of, in soils, ii, 43, 601.
 — estimation of, in urine, ii, 343.
 — free atmospheric, utilisation of, by nodule-bearing Leguminosæ, ii, 588.
 — in soils, estimation of, by Kjeldahl's method, ii, 43.
 — iodide, ii, 568.
 — liberation of, during putrefaction, ii, 224.
 — loss of, in drainage water, ii, 338.
 — loss of, in manures, ii, 181, 228.
 — nitric, estimation of, ii, 145.
 — — greater assimilability of, when recently formed, ii, 548.
 — organic, estimation of, ii, 343.
 — oxides, structure of, i, 636.
 — preparation of pure, ii, 270.
 — stereochemistry of, ii, 157.
 — tetroxide, molecular weight of, in the liquid state, TRANS., 1099.
 Nitrosamines, action of carbamide on, i, 265.
 Nitroso-compounds, action of hydrazine hydrate on, i, 701.
 Nitrous acid, conditions of the formation and decomposition of, ii, 413.
 — — detection and estimation of, ii, 298.
 — — estimation of, in sodium nitrite, ii, 43.
 — — ethereal salts of, i, 382.
 — — existence of, in aqueous solution, ii, 569.

Nitrous acid, presence of, in nitric acid, ii, 206.
 Nitrous oxide, boiling point of, at atmospheric pressure, TRANS., 833, 836.
 — — combustion of hydrogen in, ii, 113.
 — — liquid, refractive index of, ii, 201.
 — — solid, melting point of, TRANS., 836.
 Nononaphthene, derivatives of, i, 196.
 Nonylone, preparation of, TRANS., 455.
 Nonyloneoxime, TRANS., 457.
 Nucleic acid, i, 680.
 Nuclein, vegetable, i, 539.
 Nuclein-bases, i, 309.
 Nucleo-albumins, ii, 133.
 Nutrition with carbohydrate and flesh and with carbohydrate alone, ii, 327.
 Nutritive value of albumoses, ii, 539.
 — — of proteids, ii, 540.

O.

Oats, power of digestion and absorption of rabbits for, ii, 132.
 — — relative value of ammonium sulphate and sodium nitrate, as a manure for, ii, 593.
 Octane, critical constants of, ii, 446.
 — — magnetic rotation of, ii, 442.
 — — normal, molecular weight of, in the liquid state, TRANS., 1099.
 Octahydronaphthyridine, i, 688.
 Octahydronicotine, i, 375, 489.
 — — dinitroso-, i, 489.
 Octomethyltetramidophenylacridine, i, 471.
 Octonaphthenic alcohol, i, 420.
 Octonaphthylene, i, 420.
 Octylene, critical temperature of, ii, 446.
 — — magnetic rotation of, ii, 442.
 Ocylic glycerate, active, TRANS., 1413.
 Octylphenol [1 : 4], i, 216.
 Oil, cotton seed, detection and approximate estimation of, in lard and olive oil, ii, 440.
 — — — heated, detection of, in lard, ii, 603.
 — — essential, of *Andropogon schænanthus*, i, 664.
 — — of *Cochlearia armoracia*, i, 633.
 — — of coriander, i, 661.
 — — of *Eucalyptus globulus*, i, 726.
 — — of garlic, i, 103.
 — — of hops, PROC., 1893, 177.
 — — of *Mosula japonica*, thymol in, ii, 181.
 — — of niaouli, i, 523.

- Oil, essential, of onion, i, 104.
 — of paracoto bark, i, 103.
 — of the root of *Aspidium filix mas*, i, 625.
 — of the seeds of *Cicuta virosa*, i, 634.
 — extraction of, from pigments, ii, 494.
 — linseed, supposed saponification of, by Dutch white lead, *PROC.*, 1893, 122.
 — mineral, detection and estimation of neutral fats in, ii, 604.
 — detection of, in rosin oil, ii, 350.
 — of caraway, preparation of optically inactive cymene from, i, 17.
 — of pimento and of cloves, toxicological detection of, ii, 397.
 — of roses, Bulgarian (Turkish), i, 662.
 — ethyl alcohol in, ii, 181.
 — of thuja, constituents of, i, 105.
 — of turpentine, American, i, 594.
 — constitution of, i, 276.
 — French, action of picric acid on, *TRANS.*, 1388.
 — oxidation products of, *TRANS.*, 1327.
 — olive, detection and approximate estimation of cotton seed oil in, ii, 440.
 — pine needle, i, 659.
 — polei, bases from, i, 115.
 — sesame, Baudoin's test for, ii, 197.
 — spruce, i, 659.
 — Turkey-red-, i, 455.
 — wood-, constituents of, i, 558.
 Oils, action of nitrous acid on, ii, 559.
 — analysis of, ii, 603.
 — and fats, iodine absorption of, ii, 309.
 — ethereal, analysis of, ii, 560.
 — detection of cineole in, ii, 395.
 — Hübl's iodine numbers for, ii, 103.
 — rapid saponification of, ii, 603.
 Okra pods, analyses of, ii, 293.
Oldenlandia umbellata, colouring and other principles of, *TRANS.*, 1160.
 Olefines, action of nitrosyl chloride and of nitric peroxide on, *TRANS.*, 479.
 — molecular refractive power of, ii, 57.
 Oleic acid, action of sodium hydrogen sulphite and of sulphurous acid on, i, 549.
 — constitution of, i, 551.
 — estimation of, ii, 251.
 — hydrazide of, i, 231.
 Oleoricinic acid, i, 456.
 Olibanum, terpenes from, i, 190.
 Olive oil, detection and approximate estimation of cotton seed oil in, ii, 440.
 Onion, essential oil of, i, 104.
 Opianic acid, action of ammonia and hydrazine on, i, 371.
 — methylation of, i, 167.
 Opiazone, i, 371.
 — chlor-, i, 371.
 Opium smoke, i, 226.
 — physiological action of, ii, 179.
 Optical activity, relation of the ethereal salts of diacetyl glyceric acid to, *TRANS.*, 1419.
 — properties as indicative of structure, *PROC.*, 1893, 57.
 Oranges, analyses of, ii, 227.
 Orcinol, action of chlorine on, i, 259.
 — formation of, from dehydracetic acid, *TRANS.*, 122.
 — ketochlorides, conversion of, into pentene derivatives, i, 318.
 — pentachlor-, i, 259.
 — trichlor-, i, 260.
 Ores, estimation of phosphorus in, ii, 44.
 Organic analysis, ultimate, source of error in, ii, 306.
 — electrosyntheses, i, 630.
 Organic-compounds, heats of combustion of, ii, 59.
 — influence of negative groups on, i, 381.
 Organic-substances, estimation of nitrogen in, by Dumas' method, ii, 297.
 — estimation of sulphur in, ii, 187.
 Organic sulphur-compounds, i, 35.
 Organism, animal, action of phosphorus and of arsenious anhydride in the, ii, 136.
 — accumulation of potassium bromide in the, ii, 176, 217.
 — accumulation of strontium bromide in the, ii, 217.
 — behaviour of hydrolytic ferments in the, ii, 329.
 — behaviour of xylene in the, ii, 178.
 — detection of mercury in the, ii, 243.
 — fluorine compounds in the, ii, 23.
 — β -hydroxybutyric acid in the, ii, 428.
 — localisation of mercury in the, ii, 217.
 — transformations of arsenious anhydride in the, ii, 583.
 — uric acid in the, ii, 384.
 Orthochlorites, composition of, ii, 19.
 Oscine, i, 679.
 Osmic acid, ii, 381.

Osmic acid, action of hydrochloric, hydrobromic, and hydroiodic acids on, ii, 381.
 Osmium, ii, 324, 380.
 — oxide, black, ii, 380.
 Osmotic pressure, ii, 513.
 Oven, drying, ii, 162.
 Ox bile, acids of, ii, 220, 383.
 Oxalates, complex metallic, i, 552.
 — metallic, compounds of, with tungstic and molybdic anhydrides, i, 457.
 Oxalobromobutyric acid, i, 405.
 Oxalbutyrolactonic acid, i, 405.
 Oxaldi- β -naphthalide, i, 99.
 Oxalic acid, action of potassium permanganate on, i, 251.
 — anhydrous, *Proc.*, 1892, 186.
 — combination of, with titanous and stannous acids, i, 625.
 — decomposition of, by ferric salts, ii, 405.
 — decomposition of solutions of, i, 395.
 Oxalomolybdic acid, salts of, i, 626.
 Oxalostannic acid, i, 626.
 Oxalotitanic acid, i, 626.
 Oxalotungstic acid, salts of, i, 626.
 Oxalovanadic acid, salts of, i, 627.
 Oxalparatoluidide, tetranitro-, action of nitric and sulphuric acids on, *TRANS.*, 1068.
 Oxaluric acid phenylhydrazide, i, 554.
 — thio-, phenylhydrazide, i, 554.
 Oxalyl derivatives, i, 554.
 Oxalylmalonic diureide, ii, 360.
 Oxamic acid phenylhydrazide, i, 554.
 — thermochemistry of, ii, 360.
 Oxanil, trinitro-, *TRANS.*, 1066.
 Oxanilide dioxime, i, 494.
 — hexanitro-, *TRANS.*, 1063.
 — action of ammonia on, *TRANS.*, 1065.
 — decomposition of, with nitric and sulphuric acids, *TRANS.*, 1067.
 Oxazine, i, 44.
 Oxazine-dyes, i, 44.
 Oxazoles, synthesis of, from benzoin and nitriles, *TRANS.*, 469.
 Oxazolines, i, 532.
 Oxazone, i, 44.
 Oxides, fusion and volatilisation of, in the electric arc, ii, 507.
 — metallic, action of a high temperature on, ii, 167.
 Oximes, i, 355.
 — fatty, oxidation of peroxides of, i, 310.
 — isomeric fatty, constitution of, i, 188.
 — isomerism of, i, 89.

Oximido-acids, anhydriation of, i, 574.
 Oximido-group in ethers of the oximes, structure of, i, 87.
 — physiological action of, ii, 584.
 Oxindolecarboxylic acid, i, 212.
 Oxybrassicidic hydrazide, i, 552.
 Oxycellulose, i, 295.
 Oxygen and carbonic anhydride, exchange of, between plants and the atmosphere, ii, 180.
 — and hydrogen, combination of, ii, 410.
 — ignition point of admixed, ii, 203, 208, 257.
 — relative densities of, ii, 10.
 — atomic refraction of, ii, 254.
 — atomic weight of, ii, 163.
 — combustion by, ii, 412.
 — density of, ii, 453, 515.
 — diffusion of, in water, ii, 62.
 — dry, action of, on charcoal, ii, 571.
 — estimation of, in iron, ii, 388.
 — estimation of, in lead, ii, 302.
 — formation of ozone from, *TRANS.*, 938.
 — liquid, optical properties of, ii, 353.
 — refractive index of, ii, 201.
 — spectrum of, ii, 201.
 — supersaturated solutions of, in water, ii, 306.
 Oxycellulose, i, 387.
 Oxyhæmatin, i, 447.
 Oxyhæmoglobin, dissociation of, in aqueous solution; i, 616.
*Nt*₂-4-Oxynaphthindone, i, 337.
 Oxyphenometadiazines, i, 530.
 Oxypiperidine bases, i, 426.
 Oxypyridine bases, i, 426.
 Oxysparteine, derivatives of, i, 232.
 Ozone, constitution of, ii, 413.
 — formation of, at high temperatures, ii, 454.
 — formation of, from oxygen, *TRANS.*, 938.
 — influence of temperature on the formation of, ii, 317.

P.

Palladium, atomic weight of, ii, 73, 284.
 — electrolytic separation of, from iridium, ii, 97.
 — estimation of, ii, 195.
 — sulphides, ii, 475.
 Palmitic acid, action of iodine on the silver salt of, i, 391.
 — solubility of the lead salt of, in ether, i, 548.
 Palmityl- β -amyrin, i, 58.
 Palygorskite, ii, 174.

- Pancreatic juice in different animals, ii, 22.
 Pangaduine, ii, 290.
 Papaveraceæ, alkaloids of, i, 490.
 Papaverinamic acid, salts of, i, 181.
 Papaverinic acid, i, 180.
 — anhydride, i, 180.
 Paper, detection of resin in the sizing of, ii, 148.
 Parachloralose, i, 247.
 Paracoto bark, ethereal oil of, i, 103.
 Paraffin, occurrence of, in the distillate of train oil under pressure, i, 493.
 Paraffins, Köhlein's method of preparing, i, 681.
 — molecular refractive power of, ii, 57.
 — mononitro-, synthesis of, i, 242.
 Paragalactan, ii, 139.
 Paralactoaraban, ii, 139.
 Paraldehyde and metaldehyde, transformations of, i, 64.
 — molecular weight of, in the liquid state, TRANS., 1100.
 Paraleucaniline, action of formaldehyde on, i, 573.
 Paramagenta, i, 572.
 Paranthracene, i, 357.
 Paranthrite from Clay Co., N. Carolina, ii, 278.
 Parasaccharin, i, 546.
 Passive state of iron and steel, ii, 16.
 Peaches, Californian, analyses of, ii, 140.
 Pear, morphology of the lævulactic ferment of the, TRANS., 1263.
 — pectose, sugar from, i, 248.
 Pears, chemical composition of, ii, 37.
 Pectinose, ii, 180.
 Pectose, pear-, sugar from, i, 248.
 Penfieldite, ii, 76.
Penicillium glaucum, ferment in, resembling emulsin, i, 744.
 Pentacetylgluconitrile, i, 293.
 Pentaglycerol, i, 617.
 Pentahydroxyanthraquinolinequinone, i, 671.
 Pentahydroxypimelic acid, i, 148.
 Pentamethenylene and its dibromide, i, 557.
 Pentamethylenamine, i, 556.
 Pentamethylene, i, 556.
 Pentamethyleneauramine, i, 473.
 Pentamethylenecarboxylic acid, i, 557.
 — synthesis of, i, 694.
 Pentamethylene-derivatives, synthesis of, i, 253.
 Pentamethylenedicarboxylic acid, i, 695.
 Pentamethylenic alcohol, i, 556.
 — nitrile, i, 557.
 Pentane, critical constants of, ii, 446.
 — heat of vaporisation of, ii, 446.
 Pentane, magnetic rotation of, ii, 442.
 — secondary nitro-, i, 243.
 — specific volume and thermal expansion of, TRANS., 274.
 — tertiary nitro-, i, 243.
 Pentene-derivatives, conversion of, into indene-derivatives, i, 344.
 Penterythritol, i, 617.
 Pentethylbenzene, i, 409.
 Pentiazolines, i, 427.
 Pentine, specific volume and thermal expansion of, TRANS., 277.
 Pentosans, estimation of, in vegetables, ii, 52.
 — in plants, ii, 430.
 Pentoses, estimation of, in vegetables, ii, 52.
 — in urine, ii, 110.
 — soluble, in plants, i, 247.
 — physiological action of, ii, 427.
 Pentylenic acids, isomeric, i, 689.
 Peptic digestion, influence of chloroform on, ii, 217.
 Peptone and albumoses, i, 233, 741.
 — cryoscopy of, i, 680.
 — diffusibility of, 234.
 — estimation of, by precipitation as mercury peptonate, ii, 104.
 — estimation of the nitrogenous constituents of, ii, 146.
 Peptones, chemical constitution of, i, 235.
 — commercial, estimation of peptone in, ii, 146.
 Perchloric acid, preparation of, ii, 390.
 Perchromic acid, sodium salt of, ii, 471.
 Periodic classifications of L. Meyer and Mendeléeff, relation between, ii, 513.
 — law, ii, 267.
 — system, specific gravity of the elements in, ii, 513.
 — table of the elements, TRANS., 852.
 Permeability of precipitated membranes, ii, 367.
 Petroleum, acids occurring in, i, 268.
 — Californian, i, 237.
 Phellonic acid, ii, 181.
 Phenacyl bromide and benzylamine, interaction of, TRANS., 1355.
 Phenacylacetylacetone, action of nitric acid on, i, 196.
 Phenacylbenzylamine, TRANS., 1362.
 — preparation of, TRANS., 1359.
 — salts of, TRANS., 1360.
 Phenacyldeoxycuminoïn, i, 219.
 Phenacyldeoxypiperonoïn, i, 219.
 Phenanthramidotertiarybutylphenazine, i, 637.
 Phenanthrapiazine, 1 : 4-dihydride, TRANS., 1286.
 Phenanthraquinone, diamido-, substantive cotton dyes from, i, 422.

- Phenanthraquinone, reduction and simultaneous acetylation of, TRANS., 771.
 — reduction of, with hydriodic acid, TRANS., 770.
 — reduction of, with zinc and hydrochloric acid, TRANS., 772.
 Phenanthraquinonedisazo- α -naphthol, i, 422.
 Phenanthraquinonedisazo- β -naphthol, i, 422.
 Phenanthraquinonedisazo- β -naphthylamine, i, 422.
 Phenanthraquinonedisazoresorcinol, i, 422.
 Phenanthrene, action of nitric peroxide on, TRANS., 1893.
 — as a solvent in cryoscopic investigations, ii, 512.
 Phenanthridine benzochloride, i, 722.
 — benzyl chloride, i, 722.
 — chloro-, i, 658.
 — ethiodide, i, 722.
 — ethohydroxide, i, 722.
 — oxidation of, i, 722.
 Phenanthridone, i, 658, 722.
 Phenanthronitrotertiarybutylphenazine, i, 637.
 Phenazine, action of alkylid iodides on, i, 283.
 Phenazones, i, 733.
 Phenetidine, parathionyl-, i, 517.
 Phenetoil, action of phenylthiocarbimide on, i, 154.
 Phenetoilsulphonic acids, isomeric change in, PROC., 1892, 214.
 Pheno-2 : 3-dimethyldihydrometadiazine, i, 609.
 Pheno-2 : 4-dimethyldihydrometadiazine, i, 609.
 Pheno-2' : 4'-diphenylmetadiazine, i, 49.
 Pheno-2'-ethyl-4'-phenylmetadiazine, i, 48.
 Pheno-2'-isopropyl-4'-phenylmetadiazine, i, 49.
 Phenol, bromochloroamido- [2 : 6 : 4], i, 321.
 — bromochloronitro-[2 : 6 : 4], i, 321.
 — compound of, with aluminium chloride, i, 508.
 — compounds of alkali phenoxides with, i, 409.
 — dibromoparamido-, i, 719.
 — dinitro- [2 : 4], i, 19.
 — ethers, action of, on thiocarbimides, i, 154.
 — — heats of combustion of, ii, 59.
 — — hydrolysis of, by means of aluminium chloride, i, 152.
 — homologues of, i, 563.
 — metamido-, and its derivatives, i, 265.
 — nitration of, at low temperatures, i, 460.
 Phenol, orthamido-, action of chlorine on, i, 698.
 — orthonitro-, action of ethylenediamine on, i, 699.
 — volumetric estimation of, in urine, ii, 100.
m-Phenolazo- α -naphthylamine, PROC., 1893, 127.
 Phenoleucalyptolmethane, metanitro-, i, 726.
 Phenolphthalein bisphenylcarbamate, i, 419.
 — constitution of, i, 273.
 — nitro-derivatives of, PROC., 1893, 14.
 Phenolphthaleinoxime, tetrabromo-, i, 719.
 Phenols, action of chlorine on, i, 259, 317.
 — action of, on ketones, i, 214.
 — amido-, action of sodium sulphite on salts of, i, 568.
 — — condensation of, with aldehydes and ketones, i, 78.
 — — condensation products of, i, 273.
 — — preparation of, from their salts, i, 568.
 — behaviour of thiocarbonates towards, i, 75.
 — estimation of, in crude carbolic acid, ii, 394.
 — heats of combustion of, ii, 59.
 — nitro-, action of ethylenediamine on, i, 699.
 — synthesis of, from ethylic acetate, i, 697.
 Phenometadiazine, derivatives of, i, 47, 530, 531, 609.
 Phenometadiazines, oxidation of, i, 532, oxy-, i, 530.
 Pheno-2-methyldihydrometadiazine, i, 609.
 Pheno-2'-methyl-4'-phenylmetadiazine, i, 47.
 Pheno-4'-phenylmetadiazine picrate, i, 49.
 Pheno-4'-phenylmetadiazine-2'-carboxylic acid, i, 49.
 Pheno-2'-propyl-4'-phenylmetadiazine, i, 48.
 β -Phenotriazyl α -methyl ketone, i, 158.
 Phenoxides of the alkalis, i, 316.
 γ -Phenoxybutyramidine thiosulphate, i, 9.
 γ -Phenoxybutyrothiamide, i, 9.
 Phenoxyorthotoluonitrile, i, 16.
 Phenyl isobutyl ketoxime, i, 163.
 Phenylacetamidoacetophenone, i, 532.
 Phenylacetic acid, action of heat on, i, 512.
 — — action of phenylhydrazine on, PROC., 1892, 219.

- Phenylacetic acid, dithio-, i, 141.
 ——— orthobromoisoinitroso-, i, 96.
 Phenylacetoglycollic acid, lactonic acid of, i, 280.
 Phenylacetylene diiodide, i, 18.
 Phenylacridine, i, 718.
 ——— diamido-, action of formaldehyde on, i, 573.
 Phenylacrylamide, i, 696.
 Phenylamidolactic acid, new, from glycocine and benzaldehyde, i, 166.
 Phenyl- β -amidolactic acid, i, 36.
 Phenylamidoquinoline, i, 728.
 Phenylanilcyanamide, i, 206.
 Phenylanilidolactic acid, i, 37.
 Phenylanilidothiobiazolone, i, 28.
 Phenylanthranilic acid, 1 : 3 : 6-amido-, i, 650.
 ——— preparation of, i, 650.
 Phenylatronic acid, i, 692.
 Phenylazimidosalicylic acid, nitro-, i, 211.
 Phenylazoformazyl, i, 83, 85.
 Phenylazomethylsotriazone, i, 158.
 Phenylbenzenesulphonic acid, thio-, i, 416.
 Phenylbenzhydrylaminethiocarbamide, i, 704.
 Phenylbenzimidophenyl ether, i, 409.
 Phenylbenzylhydrazinesuccinic acid, i, 371.
 Phenylbenzylphenylbenzenylamidine, i, 204.
 3 : 1-Phenylbenzylphthalazone, i, 522.
 Phenylbenzylpiperazone, i, 370.
 Phenylbenzylpyrazolidine, i, 612.
 Phenylbromacetylpyrazole, i, 179.
 Phenylbutylthiourea, secondary, TRANS., 322.
 Phenylcampholythiocarbamide, i, 109.
 Phenylcamphoramidic acid, i, 362.
 Phenylcarbazacridine, oxidation of, i, 417.
 Phenylcarboxytolylpropionic acid, i, 513.
 Phenyl- β -chlorolactic acid, i, 36.
 1-Phenylchloropyrazole, i, 672.
 2'-Phenylcinchoninic acid methiodide, and other metho-salts, i, 731.
 ——— methylbetaine, i, 731.
 α -Phenylcinnamic acid, i, 341.
 3' : 4'-Phenyleyanisocoumarin, i, 228.
 Phenyldiamidometadiazine hydrochloride, i, 369.
 Phenyldiamidonaphthalene, i, 276.
 Phenyldiazoimide, formation of, TRANS., 256.
 ——— nitration of, TRANS., 257.
 Phenyldibenzylthiourea, TRANS., 539.
 Phenyldibromopropionic acid, separation of, into its optically active modifications, i, 93.
 Phenyldibromopropionic acid, specific rotatory power of, i, 268.
 Phenyldicarboxyphenylpropionic acid, i, 514.
 Phenyldichlorometadiazine, i, 369.
 1'-Phenyldihydroisoquinoline, i, 608.
 1-Phenyl-3 : 4-dimethylpyrazole, i, 673.
 1-Phenyl-3 : 5-dimethylpyrazole, reduction of, i, 177, 178.
 Phenyldimethylpyrimidine, i, 735.
 Phenyldimethylquinolinethiocarbamide, i, 605.
 1-Phenyl-3 : 4-dimethyltetrahydropyrazole, i, 673.
 Phenyldithiobiuret, i, 575.
 ——— constitution of, i, 341.
 α -Phenyldithiobiuret, oxidation of, i, 575.
 α -Phenyldithiodimethylketuret, i, 575.
 α -Phenyldithiophenylalduret, i, 575.
 o -Phenylenediacetoneitrile, reduction of, i, 267.
 Phenylenediamine, derivatives of, i, 638.
 m -Phenylenediamine, thionyl-, i, 518.
 p -Phenylenediamine, thionyl-, i, 518.
 o -Phenylenediethyldiamine, i, 267.
 o -Phenylenediethylimide, i, 267.
 m -Phenylenediimidopropyl methyl ketone, i, 605.
 p -Phenylenediimidopropyl methyl ketone, i, 604.
 o -Phenylenethiocarbamide, i, 638.
 1-Phenyl-5-ethoxypyrazole, i, 368.
 1-Phenyl-5-ethoxypyrazole-3-carboxylic acid, i, 368.
 Phenylethylacetamide, i, 608.
 Phenylethylacetylene diiodide, i, 2.
 Phenylethylamine, α -orthamido-, i, 609.
 α -Phenylethylamine α -phenylethylthiocarbamate, i, 703.
 ——— thionyl-, i, 703.
 β -Phenylethylamine, thionyl-, i, 703.
 ω -Phenylethylamine, i, 608.
 Phenylethylbenzamide, i, 608.
 Phenylethyldimethylpyrazole, i, 672.
 Phenylethylformamide, i, 608.
 n -Phenylethylorthonaphthylenediamine, i, 284.
 Phenylethylpiperazone, i, 370.
 α -Phenylethylthionamic acid, i, 703.
 β -Phenylethylthionamic acid, i, 703.
 Phenylglycidic acid, i, 36.
 Phenylglyoxylic acid, orthonitro-, reactions of, i, 469.
 Phenyl-group, introduction of, into cycloïd compounds, i, 701.
 Phenylhydrazidoisobutyronitrile and the products of its hydrolysis, i, 85.
 Phenylhydrazidosuccinamide, i, 632.
 Phenylhydrazine, action of ethylenic bromide on, i, 571.

- Phenylhydrazine, action of magnesium on, *Proc.*, 1893, 80.
- action of, on lactones, i, 473.
- action of, on mono- and di-carboxylic acids at high temperatures, *Proc.*, 1892, 219.
- action of, on some isomeric aldioximes, i, 87.
- bromination of, i, 155, 705.
- campholenate, i, 661.
- compounds of, with metallic salts, i, 267.
- metachloro-, and its salts, *Trans.*, 869.
- metadibromo-, and its derivatives, i, 155.
- orthochloro-, salts of, *Trans.*, 868.
- orthodibromo-, and its derivatives, i, 155.
- parachloro-, *Trans.*, 872.
- paranitro-, i, 155.
- preparation of unsymmetrical derivatives of, i, 411.
- salts and derivatives of, i, 154.
- sodio-, action of carbonyl chloride on, i, 24.
- Wessel's dicarbo-base from, i, 461.
- and carbodiphenylimide, i, 461.
- Phenylhydrazines, chlorinated, *Trans.*, 868.
- Phenylhydrazinesuccinylhydrazide, i, 231.
- Phenylhydrazinesulphonic acid, paranitro-, salts of, i, 156.
- Phenylhydrazocitrazinic acid, *Trans.*, 1042.
- Phenylhydrazoneacetone, paranitro-, i, 522.
- Phenylhydrazones, stereochemical, i, 208.
- Phenylhydrazo- γ -quinaldine, i, 727.
- Phenylhydrocarvylcarbamide, i, 596.
- Phenylhydrocarvylthiocarbamide, i, 596.
- Phenylhydroxyacrylic acid, i, 36.
- Phenyl- α -hydroxyerotic acid, i, 342.
- Phenylhydroxyvitamalic acid, salts of, i, 714.
- 1-Phenyl-5-hydroxypyrazolecarboxylic acid, i, 368.
- Phenylhydroxytriketone, diparabromo-, i, 171.
- Phenyllic acetylsalicylate, i, 514.
- amidophosphates, i, 315.
- benzoate, compound of, with aluminium chloride, i, 508.
- β -chloropropionate, i, 688.
- dibromosalicylate, i, 514.
- diiodofumarate, i, 397.
- ethers, amido-, condensation of, with aldehydes and ketones, i, 78.
- hippurate and its condensation products, i, 579.
- Phenyllic iodochloride, orthonitro-, i, 561.
- iodochromate, i, 505.
- iododichloride, orthochloro-, i, 506.
- reactions of, i, 256.
- salicylate phenylcarbamate, i, 514.
- silicate, action of phosphorus oxychloride on, i, 74.
- titanate, i, 257.
- Phenylimidouracil, i, 369.
- Phenylindole dibromide, tetrabromo-, i, 169.
- Phenylindoxazen, i, 95.
- dinitro-, i, 95.
- preparation of, i, 469.
- α -Phenylindoxazen, synthesis of, i, 587.
- Phenyliodoacetylene, i, 19.
- Phenylisocamylthiourea, *Trans.*, 324.
- Phenylisobutylthiourea, *Trans.*, 320.
- Phenylisoxazolonimide, i, 315.
- Phenylitaconic acid, dry distillation of, i, 190.
- Phenyl- γ -keto- α -hydroxybutyric acid, i, 302.
- Phenylmercaptothiazole, i, 634.
- l*-Phenylmenthylthiocarbamide, i, 724.
- r*-Phenylmenthylthiocarbamide, i, 725.
- Phenylmetadimethoxyphenylmethane, metanitro-, i, 216.
- Phenylmethahydroxymethoxyphenylmethane, metanitro-, i, 216.
- Phenylmethylacetylpyridonone, i, 400.
- Phenylmethylbenzylbenzenylamidine, i, 205.
- 1-Phenyl-3-methyl-5-ethoxypyrazole, i, 368.
- 1 : 4 : 5-Phenylmethylethylpyrazole, reduction of, i, 177.
- Phenylmethylhydrastylthiocarbamide, i, 118.
- n*-Phenylmethylorthonaphthylenediamine, i, 284.
- Phenylmethylorthopiperazone, i, 705.
- Phenylmethyloxybiazolonone, dinitro-, i, 534.
- paramido-, i, 534.
- paranitro-, and its decomposition products, i, 534.
- p*-Phenylmethyloxybiazolonecarbamide, i, 534.
- p*-Phenylmethyloxybiazolonethiocarbamide, i, 534.
- Phenylmethyloxyquinoline, i, 532.
- Phenylmethylpiperazone, i, 370.
- 1-Phenyl-3-methylpyrazole, dichloroplato-, i, 674.
- 1-Phenyl-4-methylpyrazole, i, 672.
- dichloroplato-, i, 672.
- methiodide, i, 672.
- 1-Phenyl-3-methylpyrazole-4-carboxylic acid, i, 673.
- 1-Phenyl-4-methylpyrazole-3-carboxylic acid, i, 674.

- 1-Phenyl-5-methylpyrazole-3-carboxylic acid, i, 610.
 Phenylmethylpyrazolidine, i, 612.
 Phenylmethylpyrazolidone [1 : 3 : 5], derivatives of, i, 229.
 Phenylmethylpyrazoline, i, 230.
 1 : 3-Phenylmethylpyrazoline, oxidation of, i, 229.
 α -Phenylmethylthiosemicarbazide, i, 27.
 1-Phenyl-3 : 6-orthopiperazone, i, 370.
 Phenylorthotoluylenediamine, i, 340.
 Phenylloxamide, trinitro-, and its potassium derivative, TRANS., 1065.
 α -Phenyl-naphthylene, preparation of, TRANS., 1185.
 — properties of, TRANS., 1190.
 Phenyl-naphthalenes, i, 522; TRANS., 1185.
 β -Phenyl-naphthoic acid, i, 594.
 Phenylparaphenetidine, orthamido-, and its derivatives, i, 328.
 — orthonitro-, i, 328.
 Phenylparaphenylmethyloxybiazolonethiocarbamide, i, 534.
 α -Phenylparatolylthiosemicarbazide, i, 27.
 μ -Phenylpenthiazoline, i, 427.
 Phenyl- α -phenylethylcarbamide, i, 703.
 Phenylphenylorthophenylenediamine, dinitro-, i, 199.
 Phenylphenylthiosemicarbazide, meta-chloro-, TRANS., 870.
 Phenylphthalazonecarboxylic acid, i, 476.
 Phenylphthalimide, trinitro-, i, 515.
 Phenylpropionic acid, derivatives of, i, 164.
 — chloride, i, 164.
 Phenylpropionic acid, action of phenylhydrazine on, PROC., 1892, 220.
 Phenylpropylamine, i, 702.
 — phenylpropylthionamate, i, 702.
 Phenylpropylphenylthiocarbamide, i, 702.
 Phenylpropylthionamic acid, i, 702.
 Phenylpropylthionylamine, i, 702.
 1-Phenylpyrazole, dibromo-, i, 673.
 — methiodide, i, 672.
 — synthesis of homologues of, i, 672.
 4-Phenylpyrazole, i, 281.
 5-Phenylpyrazole, i, 282.
 1-Phenylpyrazole-3 : 4-dicarboxylic acid, i, 674.
 1-Phenylpyrazole-4 : 5-dicarboxylic acid, i, 673.
 2-Phenyl- β -pyrazoledicarboxylic acid, i, 281.
 4-Phenylpyrazole-3 : 5-dicarboxylic acid, i, 281.
 5-Phenylpyrazole-3 : 4-dicarboxylic acid, i, 282.
 1-Phenylpyrazoles, substituted, reduction of, i, 673.
 Phenylpyrazolidine, i, 611.
 Phenylpyrazolidonecarboxylic acid [1 : 5 : 3], i, 231.
 5-Phenylpyrazoline, i, 282.
 5-Phenylpyrazoline-3 : 4-dicarboxylic acid, i, 282.
 Phenylpyruvic acid, i, 36.
 Phenylresinduline, B_2 -4-amido-, i, 335.
 Phenylsemicarbazide, metachloro-, TRANS., 870.
 — parachloro-, TRANS., 872.
 Phenylserine, i, 167.
 Phenylsulphoneanilide, i, 416.
 Phenylsulphonethylanilide, i, 416.
 Phenylsulphonehexahydronicotine, i, 443.
 Phenylsulphonemethylanilide, i, 416.
 Phenylsulphoneoxysulphobenzide, i, 416.
 Phenyltetrahydroisoquinolylcarbamide, i, 529.
 Phenyltetrahydroisoquinolylthiocarbamide, i, 529.
 Phenyltetrahydropyrimidine, i, 735.
 Phenyltetraketone hydrate, diparabromo-, i, 171.
 Phenylthiophen, i, 701.
 Phenylthiosulphuric acid, non-existence of Stenhouse's, i, 416.
 Phenylthiouracil, i, 369.
 Phenyltolylpropionic acid, i, 513.
 Phenylturranosazone, i, 618.
 Phenyluracil, i, 369.
 Phenylurazole, metachloro-, TRANS., 871.
 Phenylxylpropionic acid, i, 513.
 Phloridzin diabetes, ii, 480.
 — — in frogs, ii, 480.
 Phloroglucinol, derivatives of, i, 699.
 — triamido-, i, 699.
 — trinitroso-, action of ammonia on, i, 699.
 Phlorose, i, 384.
 Pholidolite from Sweden, ii, 174.
 Phoronic acid, formation of, from phorone, i, 304.
 Phosphate nodules, formation of, ii, 77.
 Phosphates, acid, estimation of free acids in presence of, ii, 41.
 — action of sulphur and water on, ii, 205.
 — from Florida, ii, 419.
 — of horse's urine, ii, 30.
 — precipitation of, by ammonium molybdate, ii, 45.
 — volumetric estimation of, ii, 597.
 Phosphatic rocks of animal origin, ii, 419.
 — — separation of iron from aluminium in, ii, 346.
 Phospholutedungstic acid and its salts, ii, 472, 574.

- Phosphomolybdates, ii, 282.
- Phosphomolybdic acid and its salts, ii, 472, 574.
- Phosphoric acid, amido-, i, 316.
- — — and its alkali salts, electrical conductivities of, ii, 357.
- — — constitution of, ii, 60.
- — — effect of work on the excretion of, ii, 583.
- — — estimation of, ii, 48, 88, 99, 185, 236, 237, 238, 299, 389, 434, 489, 490, 597.
- — — estimation of, as magnesium pyrophosphate, ii, 236, 489.
- — — estimation of, by Spica's process, ii, 299.
- — — estimation of, in basic slag, ii, 88, 238.
- — — estimation of, in slags, ii, 597.
- — — estimation of, in wine, ii, 389.
- — — pure, preparation of, ii, 272.
- — — rôle of, in the production of albumin in plants, ii, 224.
- — — soluble, citric and molybdate methods of estimating, ii, 237.
- — — soluble, in superphosphates, ii, 549.
- — — source of error in the estimation of, by magnesia mixture, ii, 185.
- — — source of error in the estimation of, in urine, ii, 99.
- — — thermal value of the three acid functions of, ii, 60.
- — — volumetric estimation of, ii, 48, 490.
- Phosphoric anhydride, preparation of, free from lower oxides of phosphorus, *TRANS.*, 473.
- — — ethylanilide, i, 324.
- — — α -naphthalide, i, 324.
- — — β -naphthalide, i, 324.
- — — orthotoluidide, and its bromo- and nitro-derivatives, i, 323.
- — — thio-, i, 324.
- — — paratoluidide, and its bromo- and nitro-derivatives, i, 324.
- — — thio-, i, 324.
- Phosphorites, colorimetric estimation of, of, ii, 553.
- — — new type of, ii, 419.
- Phosphorus, action of, on the animal organism, ii, 136.
- — — and the lecithins during the development of the hen's egg, ii, 289.
- — — black, ii, 458.
- — — during germination, ii, 289.
- — — Emmerton's process for the estimation of, ii, 553.
- — — estimation of, by neutralising the phosphomolybdate precipitate with alkali, ii, 89.
- Phosphorus, estimation of, in iron, ii, 44, 235, 392, 554, 596.
- — — estimation of, in iron, in presence of arsenic, ii, 554.
- — — estimation of, in iron ores, slags, &c., ii, 44, 392.
- — — estimation of, in soils, ii, 489.
- — — estimation of, in steel, ii, 43, 44, 235, 392, 553, 596.
- — — iodosulphide, ii, 164.
- — — micro-chemical localisation of, in the tissues, ii, 135.
- — — molecular weight of, in solution, ii, 511.
- — — oxychloride, molecular weight of, in the liquid state, *TRANS.*, 1099.
- — — precipitation of, as ammonium phosphomolybdate in the presence of arsenic, ii, 236.
- — — refraction constants of, ii, 353.
- — — refraction constants of the acids of, ii, 354.
- — — red, ii, 458.
- — — crystalline nature of, ii, 457.
- — — sulphides, ii, 443, 569.
- — — trichloride, molecular weight of, in the liquid state, *TRANS.*, 1099.
- Photometric standard, phosphorescent zinc sulphide as, ii, 202.
- Photosantonio acid, derivatives of, i, 665.
- Phthalaldehydic acid, action of ammonia and hydrazine on, i, 371.
- — — hydrazone methiodide, i, 347.
- Phthalamide, symmetrical, i, 467.
- Phthalazine, i, 732.
- — — 4-chloro-, i, 346.
- — — derivatives of, i, 346.
- Phthalazone, i, 346, 372.
- Phthaldialdoxime, i, 733.
- Phthaleinoximes, i, 719.
- Phthaleins, origin of colour in, *PROC.*, 1893, 52.
- — — sulphones of, i, 94.
- Phthalic acid, compounds of, with phenols, i, 275.
- — — dichloro-, i, 653.
- Phthalide, action of phenylhydrazine on, i, 473.
- Phthalide-derivatives, conversion of, into those of $\alpha\gamma$ -diketohydrindone, i, 415.
- Phthalides, action of alkalis on, i, 644.
- Phthalimidoethylbenzylsulphone, i, 30.
- Phthalimidoethylbenzylsulphoxide, i, 30.
- Phthalimidoethylformomercaptal, i, 31.
- Phthalimidoethyl benzomercaptal, i, 30.
- — — benzylic sulphide, i, 30.

- Phthaloisimide, i, 599.
 Phthalylacetic acid, preparation of, i, 415.
 Phyllocyanin, action of potash on, i, 41.
 Phylloxanthin, i, 41.
 Physiological action of arsenic trisulphide, ii, 583.
 ——— of asparagine, ii, 27.
 ——— of atropine, ii, 222.
 ——— of chloralose, i, 247.
 ——— of cinchonamine, ii, 223.
 ——— of cocaïne, ii, 334.
 ——— of cupreïne and its derivatives, ii, 223.
 ——— of iodine compounds, ii, 222.
 ——— of isaconitine, TRANS., 451.
 ——— of opium smoke, ii, 179.
 ——— of organic oximides, ii, 584.
 ——— of parachloralose, i, 247.
 ——— of pentoses, ii, 427.
 ——— of pilocarpine, ii, 222.
 ——— of pyridine and naphthalene derivatives, ii, 544.
 ——— of quinoline, isoquinoline, and their derivatives, ii, 585.
 ——— of sugar, ii, 584.
 ——— of the two isomeric ethylic thiocarbamates, ii, 584.
 ——— of uric acid, ii, 585.
 ——— meaning of the root nodules of *Eleagnus angustifolius*, ii, 33.
 Physiology of the embryonic heart, ii, 424.
 Piazine-derivatives, TRANS., 1284, 1293.
 ——— syntheses of, TRANS., 1355.
Picea vulgaris, oil from the needles and twigs of, i, 659.
 Picene, i, 594.
 ——— constitution of, i, 594.
 Picenic acid, i, 594.
 α -Picolyl methyl ketone, i, 43.
 2:6-Picolylacrylic acid, i, 527.
 2:6-Picolyl- α -hydroxypropionic acid, i, 527.
 2:6-Picolylactic acid, i, 527.
 α -Picolyl- β_1 -methylalkine, i, 43.
 1:6-Picolyl- ω -trichloro- α -hydroxyprop-
 ane, i, 527.
 Picric acid, combinations of, with hydro-
 carbons, TRANS., 1388.
 Picrylic titanate, i, 257.
 Pigments ground in oil, analysis of,
 ii, 494.
 ——— of Lepidoptera, i, 236.
 ——— respiratory, i, 59.
 Pilocarpine, physiological action of,
 ii, 222.
 Pimelic acid, ketone from, i, 557.
 Pimento, oil of, detection of, ii, 397.
 Pinacoline from methyl ethyl ketone,
 i, 547.
 Pinacolyl alcohol, i, 245.
 ——— chloride, i, 245.
 Pinacone and its bromo- and chloro-
 derivatives, i, 244.
 ——— bye-products of the preparation of,
 i, 543.
 Pinacone from ethyl methyl ketone,
 i, 390.
 ——— of methyl ethyl ketone, action of
 sulphuric acid on, i, 547.
 Pine needle oils, i, 659.
 ——— twig oil, i, 659.
 Pinene, absorption of bromine by,
 i, 358.
 ——— picric acid compound of, TRANS.,
 1388.
Pinus pumilio, oil of, i, 659.
 ——— *sylvestris*, pine needle oil from,
 i, 65, 660.
 β -Pipcoline, resolution of, into its
 optical isomerides, i, 427.
 Pipcolinecarboxylic acid, i, 176.
 Piperazine, i, 374; PROC., 1893, 35.
 Piperazine-group, i, 54.
 Piperazines, i, 486, 675, 729.
 Piperidine, action of hydriodic acid on,
 i, 174.
 ——— action of, on haloïd salts of cad-
 mium, i, 43.
 ——— action of, on haloïd salts of mer-
 cury, i, 174.
 ——— dichloryl-, i, 192.
 ——— mercuriochloride, i, 174.
 ——— mercuriodide, i, 175.
 ——— molecular weight of, in the liquid
 state, TRANS., 1101.
 Piperidine-bases, action of hydrogen
 peroxide on, i, 113.
 ——— of the β -series, i, 602.
 Piperidondine-orthamidobenzyllic alco-
 hol, i, 24.
 δ -Piperidylbutylamine, i, 9.
 γ -Piperidylbutyric acid, i, 9.
 γ -Piperidylbutyronitrile, i, 9.
 Piperidyltetrahydronaphthylalkine,
 i, 592.
 Plagioclase in a Minnesota gabbro,
 ii, 78.
 Plant cells, green, assimilation of form-
 aldehyde by, ii, 32.
 Planté cell, chemistry of, ii, 3, 4.
 Plants, absorption of atmospheric nitro-
 gen by, ii, 84, 138, 236, 590.
 ——— action of solutions of ferrous
 sulphate on, ii, 143.
 ——— and the atmosphere, interchange of
 carbonic anhydride and oxygen be-
 tween, ii, 137, 180.
 ——— are nitrates indispensable for the
 growth of?, ii, 385.
 ——— assimilation of nitrogen by, ii, 33,
 590.

- Plants, chlorophyllous, assimilation of carbonic anhydride by, ii, 483.
 — detection of carotene in, ii, 33.
 — estimation of fluorine in the ash of, ii, 234.
 — fixation of free nitrogen by, ii, 336, 590.
 — fodder, Swedish, ii, 592.
 — occurrence of iron in, ii, 484.
 — pentosans in, ii, 430.
 — production of albumin in, ii, 224.
 — soluble pentoses in, i, 247.
- Plasmic acid, i, 680.
- Platiniferous nickel ore from Canada, ii, 286.
- Platinodiamine iodochloride, ii, 127.
- Platinous chloride, preparation of, PROC., 1893, 38.
- Platinum, action of hydrochloric acid on, under pressure, ii, 169.
 — action of silicon on, ii, 474.
 — ammoniacal compounds of, ii, 127.
 — detection of, ii, 192.
 — electrolytic separation of, from iridium, ii, 97.
 — estimation of, by electrolysis, ii, 305.
 — fusion and volatilisation of, in the electric arc, ii, 508.
 — refining of, ii, 17.
- Platinum-compounds, basic new, i, 364.
- Platodiamine chloride, ii, 127.
- Platopyrazole compounds, i, 674.
- Platososemiamine platosodiethylamine chloride, i, 364.
 — platosodipyridine chloride, i, 364.
- Platososemiethylamine platosodiamine chloride, i, 365.
 — platosodipyridine chloride, i, 365.
- Platososemipyridine platosodiamine chloride, i, 364.
 — platosodiethylamine chloride, i, 365.
 — platosodipyridine chloride, i, 365.
 — potassium chloride, i, 365.
- Plattnerite from Idaho, ii, 75.
- Plums, Californian, analyses of, ii, 591.
- Poisoning by hydrogen sulphide, ii, 83.
 — by sulphuric acid, ii, 335.
- Polei oil, bases from, i, 115.
- Pollen, colouring matter of, ii, 139.
- Polybasite from Aspen, Colorado, ii, 75.
- Polyporus igniarius*, new acid from, i, 602.
- Polyricinic acid, i, 456.
- Polysalicylide, i, 166.
- Populus tremula*, tar from the bark of, i, 454.
- Potassammonium, action of oxygen on, ii, 462.
 — action of carbonic oxide on, ii, 520.
 — molecular weight of, ii, 115.
- Potassium aluminate, decomposition of, by carbonic anhydride, ii, 279.
 — decomposition of, in presence of alumina, ii, 278.
 — ammonium molybdo-sulphite, ii, 530.
 — and sodium chlorides, rate of evaporation of solutions of, ii, 64.
 — direct estimation of, by means of tartaric acid, ii, 598.
 — antimonites, ii, 171.
 — bromide, accumulation of, in the organism, ii, 176, 217.
 — bromopyroselenite, ii, 318.
 — carbonate, formation of, in nature, ii, 165.
 — carbonyl, ii, 520.
 — chlorate, criticism of Stas' fundamental determinations on, ii, 163.
 — chloride, boiling points of aqueous solutions of, ii, 260.
 — chromium malonate, ii, 314.
 — cobaltous sulphate, crystallography of, TRANS., 388.
 — copper sulphate, crystallography of, TRANS., 396.
 — dextromethoxysuccinate, TRANS., 224.
 — dichromate, action of nitric acid on, ii, 16.
 — estimation of, ii, 46, 190, 300, 344, 390, 436, 522.
 — estimation of, as perchlorate, ii, 46, 190, 390.
 — estimation of, by the Lindo-Glad-ding process, ii, 344, 436.
 — estimation of, in presence of non-volatile acids, ii, 390.
 — ferrate, ii, 161.
 — ferricyanide, gas-volumetric estimation of, ii, 98.
 — ferrite, ii, 169.
 — ferrocyanide, action of dilute acids, &c., on, ii, 393.
 — and ferricyanide, volumetric analyses by means of, ii, 242.
 — ferrous sulphate, crystallography of, TRANS., 365.
 — flame spectrum of, ii, 402.
 — fluoroxypemobate, ii, 213.
 — fluoroxypertantalate, ii, 213.
 — fluoroxypertungstate, ii, 213.
 — glycerate, active and inactive, TRANS., 303.
 — hydrogen dextroethoxysuccinate, TRANS., 236.
 — dextromethoxysuccinate, TRANS., 223.
 — lævomethoxysuccinate, TRANS., 227.
 — tartrate, solubility of, in dilute alcohol, i, 309.

- Potassium hydrogen tartrate, use of, in volumetric analysis, ii, 144.
- — — triplatohexanitrite, electro-metric study of, ii, 256.
- — — hydroxide, action of sulphuric acid on, at very low temperatures, ii, 112.
- — — hydrates of, TRANS., 898.
- — — infra-red emission spectrum of, ii, 58.
- — — iodotetrachloride, ii, 68.
- — — iridiochloride, action of hydrogen sulphide on, 379.
- — — lead haloïds, ii, 465, 524.
- — — iodide, ii, 118.
- — — magnesium sulphate, crystallography of, TRANS., 344.
- — — — — new, from the Westeregeln salt beds, ii, 325.
- — — molybdoarsenates, ii, 282.
- — — molybdoselenite, ii, 531.
- — — molybdosulphite, ii, 530.
- — — nickelous sulphate, crystallography of, TRANS., 379.
- — — permanganate, action of sulphuric acid on, ii, 15.
- — — persulphate, molecular weight of, ii, 572.
- — — platinochloride, rapid reduction of, ii, 284.
- — — platonitrite, new, ii, 213.
- — — plumbichloride, ii, 523.
- — — seleniobromide, ii, 318.
- — — separation of magnesium from, ii, 46.
- — — silver iodide, ii, 69.
- — — tellurate, ii, 161.
- — — telluribromide, ii, 457.
- — — tellurichloride, ii, 457.
- — — telluriodide, ii, 457.
- — — tetrachromate, ii, 528.
- — — tetroxide, constitution of, ii, 413.
- — — trihaloïds, ii, 67.
- — — zinc sulphate, crystallography of, TRANS., 356.
- Potassium-astrachanite, ii, 276.
- Potatoes, amount of starch in different varieties of, ii, 430.
- — — manuring, ii, 593.
- — — migration of starch in the tubers of, ii, 485.
- Potential, difference of, at the contact of mutually reacting liquids, ii, 149.
- — — differences between acids and bases, ii, 256.
- — — — — between metals and bases, ii, 255.
- Precipitates, estimation of, by an optical method, ii, 294.
- Press for laboratory use, ii, 452.
- Pressure, combination of oxygen and hydrogen by, ii, 410.
- Pressure, determination of melting points under, ii, 563.
- — — internal, in solutions, ii, 447.
- — — osmotic, ii, 513.
- — — relation of Volta electromotive force to, ii, 256.
- Pressures, "corresponding," of certain ethereal salts, TRANS., 1244.
- Propane, heat of combustion of, ii, 444.
- — — properties of, i, 681.
- — — secondary nitro-, i, 242.
- — — triamido-, i, 31.
- Propenyl and allyl derivatives, thermochemistry of isomeric, ii, 153.
- Propionylaldoxime, modifications of, PROC., 1893, 77.
- Propionamide, α -isonitroso-, i, 503.
- Propionamidoacetophenone, i, 531.
- Propionanilide, α -bromo-, i, 51.
- Propio- α -naphthalide, α -bromo-, i, 52.
- Propio- β -naphthalide, α -bromo-, i, 52.
- Propionic acid, α -amido-, behaviour of, at high temperatures, i, 132.
- — — β -amido-, i, 631.
- — — α -bromo-, action of alcoholic potash on the anilide, toluidides, and naphthalides of, i, 51.
- — — — — preparation of, i, 65.
- — — — — diamido-, and its derivatives, i, 686.
- — — α -dibromo-, thermochemistry of, ii, 358.
- — — β -dibromo-, thermochemistry of, i, 625.
- — — — — molecular weight of, in the liquid state, TRANS., 1103.
- Propionic anhydride, specific volume and thermal expansion of, TRANS., 286.
- — — chloride, $\alpha\beta$ -dibromo-, i, 549.
- — — cyanide, dimolecular, i, 553.
- Propionitrile, molecular weight of, in the liquid state, TRANS., 1104.
- Propionylguanaine, i, 309.
- Propionylhydroxyethyl cyanide, α -dichloro-, i, 122.
- Propionylmalic acid, i, 500.
- — — anhydride, i, 500.
- l*-Propionylmenthylamine, i, 724.
- r*-Propionylmenthylamine, i, 725.
- Propionylorthamidobenzophenone, i, 48.
- Propionylorthotoluidide, α -bromo-, i, 51.
- Propionylparatoluidide, α -bromo-, i, 51.
- p*-Propoxytoluenemetasulphonamide, i, 585.
- Propyl methyl ketone, amido-, i, 734.
- Propylacetylene diiodide, i, 2.
- Propylamidophenol and its acetyl derivatives, i, 199.
- — — from camphor, i, 152, 199.

- Propylamine, freezing points of aqueous solutions of, TRANS., 165.
 — hydrates of, TRANS., 167.
 — thionyl, i, 504.
 Propylamines, preparation and properties of, i, 249.
 Propylbenzene, chloro-, i, 562.
 — critical constants of, ii, 446.
 — magnetic rotation of, ii, 442.
 — thermochemistry of, i, 562.
 Propylchloramine, i, 296.
 Propylcinnamylpyrroline, i, 227.
 Propyldichloramine, i, 296.
 Propylene, action of nitric peroxide on, TRANS., 481.
 — action of nitrosyl chloride on, TRANS., 480.
 — heat of combustion of, ii, 444.
 — symmetrical tribromo-, i, 1.
 Propylenediamine, derivatives of, i, 79.
 Propylenediorthotolylcarbamide, i, 80.
 Propylenediparatolylcarbamide, i, 81.
 Propylenediphenylcarbamide, i, 80.
 Propylenic chloride, chlorination of, i, 449.
 Propylic acetate, vapour pressure, molecular volume, and critical constants of, TRANS., 1222.
 — alcohol, depression of the freezing point of acetic acid by, TRANS., 1024.
 — — depression of the freezing point of benzene by, TRANS., 1020.
 — — depression of the freezing point of water by, TRANS., 1016.
 — — magnetic rotation of, ii, 442.
 — — molecular weight of, in the liquid state, TRANS., 1102.
 — chlorides, bromination of, i, 449.
 — β -chloropropionate, i, 688.
 — diacetylglycerate, TRANS., 1423.
 — formate, heat of vaporisation of, ii, 446.
 — — vapour pressure, molecular volume, and critical constants of, TRANS., 1211.
 — glycerate, inactive and active, TRANS., 513.
 — orthotoluate, β -amido-, i, 533.
 — paratolyl ether, γ -chloro-, i, 9.
 Propylenecacetic acid, i, 392, 689.
 Propylorthotoluamide, β -bromo-, i, 532.
o-Propylparaisopropyltoluene, i, 163.
 Propylparatoluamide, β -bromo-, i, 533.
 Propylpyrrolines, i, 226.
 Protagon, i, 234.
 Protamine, reactions of, i, 536.
 Proteid, amount of, in single red blood corpuscles, ii, 332.
 — in diet, ii, 540.
 — in exudations and transudations, ii, 334.
 Proteid, influence of sodium chloride on the digestibility and assimilation of, ii, 579.
 — origin of fat from, in the body, ii, 327.
 — reserve of asparagus root, ii, 431.
 Proteid-molecule, presence of certain groups in, i, 645.
 Proteids, behaviour of, towards concentrated hydriodic acid, i, 379.
 — colour reactions of, i, 615.
 — crystallised vegetable, i, 380.
 — filtration of, through porcelain, i, 540.
 — fractional heat coagulation of, i, 59.
 — heats of combustion of, ii, 59.
 — nutritive value of, ii, 540.
 — of egg white, i, 379.
 — of kidney and liver cells, ii, 133.
 — of linseed, ii, 292.
 — of nervous tissues, ii, 478.
 — of spleen and thyroid, ii, 425.
 — of the crystalline lens, ii, 424.
 — of wheat, i, 741.
 Protopine, i, 490.
 Prunes, Californian, analyses of, ii, 140, 591.
 Pseudobrookite as a sublimation product, ii, 18.
 Pseudobutylenediamine, derivatives of, i, 79.
 Pseudocinchonidine, i, 676.
 Pseudocinchonine, i, 678, 738.
 Pseudocodeine, salts of, i, 675.
 Pseudocumene, critical constants of, ii, 446.
 — magnetic rotation of, ii, 442.
 Pseudocumeneazo- β -naphthol, TRANS., 934.
 — reduction of the acetyl derivative of, TRANS., 934.
 Pseudohyoscyamine, i, 491.
 Pseudoinulin, i, 385.
 Pseudopelletierine, i, 287.
 Pseudopelletierineoxime, i, 287.
 Pseudoquinine, i, 56, 737.
 — salts of, i, 737.
 Pseudotropine, derivatives of, i, 58.
 Psyllostearyl alcohol, i, 125.
 Ptilolite, constitution of, ii, 77.
 — from Silver Cliff, Colorado, ii, 77.
 Ptomaine from the urine in cases of eczema, i, 614.
 Ptomaines, i, 538.
 — from the urine in erysipelas and puerperal fever, i, 183.
 Puerperal fever, ptomaines from the urine in, i, 183.
 Purpurin from *Rubia sikkimensis*, TRANS., 1158.
 Pus, glycogen in, ii, 541.

- Putrefaction, action of light in preventing, TRANS., 1109.
 — in the intestines, ii, 137.
 — liberation of nitrogen during, ii, 224.
 — ptomaines in the products of, i, 538.
 Pyogenin, i, 235.
 Pyosin, 235.
 Pyrazine, i, 373, 734.
 — derivatives of, TRANS., 1284, 1293.
 — synthesis of, i, 612.
 Pyrazinecarboxylic acid, i, 373, 487.
 Pyrazinedicarboxylic acid, i, 373.
 Pyrazines, i, 486, 612, 675, 729.
 Pyrazinetetracarboxylic acid, i, 373.
 Pyrazinetricarboxylic acid, i, 487.
 Pyrazole, iodo-, i, 432.
 — nitro-, i, 432.
 — preparation of, i, 432.
 Pyrazole-4-carboxylic acid, i, 432.
 Pyrazole-compounds, i, 671.
 Pyrazole-derivatives, i, 179.
 — from unsaturated acids and hydrazines, i, 229.
 — new synthesis of, i, 44.
 — synthesis of, i, 610.
 — synthesis of, by means of ethylic diazoacetate, i, 439.
 Pyrazole-3 : 5-dicarboxylic acid, i, 179, 431, 674.
 Pyrazoles from unsaturated acids and hydrazines, i, 231.
 Pyrazole-series, some acids of the, i, 673.
 Pyrazole-3 : 4 : 5-tricarboxylic acid, i, 432.
 Pyrazoline, i, 300.
 — reaction, i, 229.
 Pyrazoline-derivatives, reactions of, i, 430.
 Pyrazoline-3 : 5-dicarboxylic acid, i, 430.
 Pyrazoline-3 : 4 : 5-tricarboxylic acid, i, 431.
 Pyrazolonaldehyde, i, 428.
 Pyrazolone, i, 180, 428, 729.
 — derivatives of, i, 367, 729.
 — from ethylic acetylenedicarboxylate, i, 611.
 — from ethylic propiolate, i, 610.
 — isonitroso-, i, 729.
 — 4-isonitroso-, i, 428.
 Pyrazolonecarbonylbenzalhydrazine, i, 367.
 Pyrazolonecarboxylic acid, isonitroso-, i, 367.
 — silver salt of, i, 367.
 Pyrazolone-3-carboxylic acid, i, 180, 729.
 — hydrazide, i, 180.
 Pyrazolone-4-parazotoluene, i, 611.
 Pyridazolone, i, 732.
 Pyridazolone-3-carbonylbenzylhydrazine, i, 732.
 Pyridazolone-3-carbonylhydrazine, i, 732.
 Pyridazolone-3-carboxylic acid, i, 732.
 Pyridine, action of ammonium hydrogen sulphate on, i, 411.
 — action of, on haloïd salts of cadmium, i, 43.
 — alkyl iodides, action of alkalis on, i, 279.
 — amido-, i, 727.
 — amido- and nitro-derivatives of, i, 727.
 — compounds of, with lead di- and tetra-chlorides, ii, 465.
 — depression of the freezing point of benzene by, TRANS., 1020.
 — depression of the freezing point of water by, TRANS., 1018.
 — magnetic rotation of, ii, 442.
 — mercuriodide, i, 376.
 — molecular weight of, in the liquid state, TRANS., 1101.
 — physiological action of, ii, 544.
 Pyridine-bases from Messel, action of chloral on, i, 527.
 Pyridinecarboxylic acids, non-nitrogenous acids derived from, i, 114.
 Pyridine-derivatives, formation of, from unsaturated acids, TRANS., 259, 874.
 α -Pyridinuric acid, ii, 544.
 Pyridylglycerylcarboxylic acid and its lactone, i, 605.
 Pyrimidines free from oxygen, i, 735.
 Pyrites, roasted, estimation of sulphur in, ii, 187.
 Pyrogallol and benzaldehyde, condensation of, i, 472.
 — antimonites, i, 75.
 Pyromucamide, derivatives of, i, 313.
 Pyromucic acid, β -chloro- δ -nitro-, i, 314.
 — β -chloro- δ -sulpho-, i, 313.
 — δ -chloro- β -sulpho-, i, 314.
 — $\beta\gamma$ -dichloro- δ -sulpho-, i, 314.
 Pyrophosphoric acid and metaphosphoric acid, separation and estimation of, ii, 299.
 — volumetric estimation of, ii, 597.
 Pyroselenites, compounds of, with haloïds, ii, 318.
 Pyrosulphochromic hydroxide, ii, 529.
 Pyrotartaric acid, ethereal salts of, i, 252, 307.
 — etherification of, i, 251.
 — thermochemistry of, ii, 109.
 — acids, dichloro-, i, 142, 143.
 Pyroxene-group, minerals of the, ii, 130.
 Pyrroline, action of propyl alcohol on, i, 226.
 — ferrocyanide, i, 602.

- Pyrroline, valency of nitrogen in, i, 727.
 Pyrroline-acids, affinity coefficients of, i, 42.
 Pyrroline-derivatives, basic properties of, i, 602.
 Pyruvic acid, action of hydrogen sulphide on, i, 308.
 ——— and formaldehyde, lactone from, i, 628.
 ——— derivatives of, i, 552.
 ——— metachlorophenylhydrazine, TRANS., 871.
 ——— parachlorophenylhydrazine, TRANS., 873.
 ——— trichloro-, i, 308.
 ——— anilide, i, 511.
 ——— toluidides, i, 511.

Q.

- Quartz boulder in Ohio coal, ii, 78.
 Quercetin derivatives, i, 413.
 Quercitrin, composition of, i, 413.
 Quicklime, inertness of, TRANS., 821.
 Quinaldine, γ -amido-, i, 728.
 ——— physiological action of, ii, 585.
 Quinazoline, $\beta\delta$ -dichloro-, derivatives of, i, 372.
 Quinazolines, i, 49.
 Quinhydrone, action of hydrogen chloride on, i, 322.
 ——— chloro-, i, 322.
 ——— derivatives of, TRANS., 1314.
 ——— dibromo-, TRANS., 1325.
 ——— dichloro-, TRANS., 1318.
 ——— dichlorodibromo-, from paradibromoquinone and paradichloroquinol, TRANS., 1327.
 ——— from paradichloroquinone and paradibromoquinol, TRANS., 1326.
 ——— hexachloro-, TRANS., 1322.
 ——— octochloro-, TRANS., 1323.
 ——— tetrabromo-, from paradibromoquinone, TRANS., 1326.
 ——— tetrachloro-, from metadichloroquinone, TRANS., 1319.
 ——— from paradichloroquinone, TRANS., 1321.
 Quinhydrones, monochloro-, attempts to prepare, TRANS., 1316.
 Quinic acid, rotatory power of salts of, i, 644.
 Quinidine solutions, rotatory power of, ii, 106.
 Quinine, i, 676.
 ——— appearance of fluorescence in, PROC., 1893, 63.
 ——— conversion of, into isomerides, i, 56.
 ——— double salts of, i, 115.
 Quinine, estimation of, in cinchona barks, ii, 310.
 ——— estimation of, in presence of other cinchona alkaloids, ii, 199.
 ——— ethiodide, isomeride of, i, 738.
 ——— hydrobromosulphate, i, 116.
 ——— hydrochloride, action of hydrochloric acid on, i, 676.
 ——— hydrochlorophosphate, i, 116.
 ——— hydrochlorosulphate, i, 116.
 ——— hydriodosulphate, i, 116.
 ——— mercuriodide, i, 376.
 ——— methiodides, i, 181.
 ——— sulphate, analysis of, ii, 199.
 ——— transformations of, i, 737.
 Quinic acid benzylbetaïne, i, 729.
 ——— benzylbromide, i, 729.
 ——— ethobromide, i, 729.
 ——— methiodide and other metho-salts, i, 728.
 ——— methylbetaïne, i, 728.
 ——— propobromide, i, 729.
 Quinitol, iodhydrin of, i, 255.
 Quinol, action of light on, i, 642.
 ——— action of sulphuric acid on, i, 37.
 ——— azo-derivatives of, i, 571.
 ——— dibenzoate, compound of, with aluminium chloride, i, 508.
 ——— nitro-, and its derivatives, i, 640.
 Quinoline, 2-amido-, i, 670.
 ——— 1:4-amidobromo-, i, 669.
 ——— 4:1-amidobromo-, i, 669.
 ——— 4:1-amidochloro-, i, 668.
 ——— amido-derivatives of, i, 727.
 ——— ammonium bases, constitution of, i, 177.
 ——— and its derivatives, physiological action of, ii, 585.
 ——— argentocyanide, i, 279.
 ——— argento-haloïds, i, 279.
 ——— 1-bromo-, i, 668.
 ——— 1-chloro-, i, 668.
 ——— constitution of, i, 603.
 ——— 1:4-dibromo-, i, 669.
 ——— 1-iodo-, i, 669.
 ——— 2-iodo-, i, 669.
 ——— 3-iodo-, i, 669.
 ——— 4-iodo-, i, 669.
 ——— mercuriodide, i, 376.
 ——— molecular weight of, in the liquid state, TRANS., 1101.
 ——— 2-nitro-, i, 670.
 ——— 4:1-nitrobromo-, i, 669.
 ——— 4:1-nitrochloro-, i, 668.
 ——— oxidation of, by potassium permanganate, i, 44.
 ——— plumbihaloïds, ii, 465.
 ——— rules as to substitution in, i, 667.
 Quinoline-bases, addition of chloral to, i, 438.
 Quinoline-chloral, i, 438.

Quinoline-derivatives, appearance of colour in, *Proc.*, 1893, 63.
 ——— synthesis of, i, 532.
 Quinolinediazochloride, 1:4-chloro-, i, 668.
 Quinolinephenetol, i, 377.
 Quinolinephenetolildicarboxylic acid, i, 377.
 Quinolinephenol, i, 377.
 Quinolines, conversion of the indoles into, i, 603.
 Quinoline-4-sulphonic acid, 1-chloro-, i, 668.
 Quinolinic acid, action of nascent hydrogen on, i, 176.
 Quinolinium bases, i, 365.
 Quinolone-derivatives, formation of, i, 115.
 Quinone, dinitrodioxy-, i, 699.
 ——— halogen derivatives of, *TRANS.*, 1314.
 Quinone-derivatives, conversion of para- into ortho-, *Proc.*, 1893, 13.
 Quinones, action of bleaching powder and hypochlorous acid on, i, 220.
 Quinonoid compounds, limitation of colour to truly, *Proc.*, 1893, 55.

R.

Rabbits, power of digestion and absorption of, for oats, ii, 132.
 Racemic acid, thermochemistry of, ii, 109.
 Raffinose, action of boiling water on, i, 64.
 ——— estimation of, in beet sugar, i, 683.
 ——— influence of, in the formation of molasses, i, 683.
 ——— inversion of, i, 249.
 Rain, combined nitrogen in, ii, 548.
 ——— water, a new bacillus in, ii, 83.
 Rays, determination of the intensity of, ii, 401.
 Refraction, atomic, of boron, ii, 517.
 ——— of nitrogen, ii, 254.
 ——— constants and specific inductive capacities, ii, 505.
 ——— of phosphorus, ii, 353.
 ——— of the acids of phosphorus, ii, 354.
 ——— index of, study of chemical reactions in a liquid mass by means of, ii, 201.
 ——— molecular, ii, 254.
 ——— of compounds containing nitrogen, ii, 401.
 ——— of liquid oxygen, ii, 353.
 Refractions, atomic, of the elements, ii, 253.

Refractive indices of liquid oxygen, nitrous oxide, and ethylene, ii, 201.
 ——— of sulphuric acid solutions, *TRANS.*, 99.
 ——— power, molecular, for infinite wave-length of organic compounds, ii, 57.
 ——— of ethylenic oxide, *TRANS.*, 488.
 ——— of hydrogen peroxide, ii, 163.
 ——— powers for a ray of infinite wave-length, ii, 505.
 Refractometric observations, ii, 1.
 Resin, detection of, in the sizing of paper, ii, 148.
 ——— estimation of, in soap, ii, 609.
 Resins from kamala, *TRANS.*, 985, 989.
 ——— terpenes from, i, 100.
 Resinotannol and its derivatives, i, 480.
 Resorcinol, action of light on, i, 642.
 ——— benzoate, compound of, with aluminium chloride, i, 508.
 ——— condensation of monobasic acids with, i, 719.
 ——— ketochlorides, conversion of, into pentene derivatives, i, 319.
 Resorcinolbenzein, i, 719.
 ——— di-, tetra-, and penta-bromo-, i, 719.
 ——— dinitro-, i, 719.
 Resorcinoleinnamylein, i, 720.
 ——— hexabromo-, i, 720.
 Resorcinoldisazoparatoluonitrile, i, 202.
 Resorcinolhydrocinnamylein, tetra-bromo-, i, 720.
 Resorcinolphenylacetein, i, 720.
 ——— pentabromo-, i, 720.
 ——— tetrabromo-, i, 720.
 ——— tetranitro-, i, 720.
 Resorption, influence of increased or diminished consumption of food, and of the salts added to food, on, ii, 132.
 Respiration, human, absorption of oxygen and formation of carbonic anhydride in, ii, 20.
 ——— in fishes, ii, 81.
 Respiratory globulin in the blood of Chitons, i, 60.
 ——— interchange, action of fatiguing muscular work on, ii, 21.
 ——— and exercise, ii, 579.
 ——— pigments, i, 59.
 Retene, action of the compound of benzoic chloride and aluminium chloride on, i, 579.
 Rhamnose, birotation and hydrazone formation of, i, 126.
 ——— fermentation of, with a lævoflactic ferment, *TRANS.*, 1279.

- Rhamnose, molecular weight of, ii, 406.
 — specific rotatory power of, i, 126.
 Rhodinol, constitution of, i, 661.
 Rhodium chloronitrate, ii, 213.
 Ricinic acid, i, 456.
 Ricinoleic acid, action of sulphuric acid on, i, 455.
 Ricinosulphuric acid, i, 455.
 Rings, five-membered, i, 426.
 Rock salt from Deésakna, ii, 575.
 Rocks, acid eruptive, constitution of spherulites in, ii, 287.
 — estimation of ferric oxide in, ii, 243.
 — volcanic, from Gough's Island, South Atlantic, ii, 539.
 Root nodules of *Eleagnus angustifolius*, physiological meaning of the, ii, 33.
 Rosaniline, action of formaldehyde on, i, 573.
 — hydrochloride, action of ammonia on, i, 640.
 — hydrocyano-, constitution of, i, 711.
 — spectro-photometric investigation of the salts of, i, 333.
 Rosaniline-group, constitution of colouring matters of the, i, 640.
 Rosanilines, acid salts of, i, 332.
 — constitution of, i, 332.
 Rosindulines, i, 333.
 Roseol, i, 662.
 Roses, oil of, Bulgarian (Turkish), i, 662.
 — — ethyl alcohol in, ii, 181.
 Rosin oil, examination of, ii, 350.
p-Rosotoluidine, TRANS., 1396.
 Rotation, optical, alteration of the sign of, ii, 255.
 Rotatory power, influence of organic solvents on, ii, 562.
 — of a substance belonging to a homologous series, ii, 561.
 — of ethereal salts of acidyl-tartaric acids, i, 73.
 — — of valeric and glyceric acids, ii, 561.
 — of liquids, influence of temperature on, ii, 255, 354.
 — — variations in, i, 457.
 — of salts of the diamines, ii, 105, 106.
 — of solutions, ii, 106.
 — powers of fenchylamine and menthylamine derivatives, i, 725.
 Rottlerin, TRANS., 979.
 — action of acetic anhydride on, TRANS., 980.
 — action of nitric acid on, TRANS., 982.
 — decomposition of, with fused alkalis, TRANS., 981.
 Rottlerin, oxidation of, by hydrogen peroxide, TRANS., 982.
 Roussin's salt, ii, 211.
 Rubber goods, analysis of, ii, 399.
Rubia sikkimensis, colouring principles of, TRANS., 1157.
 Rubiadin, TRANS., 973.
 — constitution of, TRANS., 1137, 1141.
 Rubiadinglucoside, TRANS., 969.
 — behaviour of, towards phenylhydrazine, TRANS., 1140.
 — constitution of, TRANS., 1137, 1140.
 Rubidium arsenic haloïds, ii, 572.
 — aurobromide and aurochloride, ii, 68.
 — borates, ii, 460.
 — cadmium sulphate, crystallography of, TRANS., 407.
 — cobaltous sulphate, crystallography of, TRANS., 390.
 — copper sulphate, crystallography of, TRANS., 400.
 — ferrous sulphate, crystallography of, TRANS., 367.
 — flame-spectrum of, ii, 402.
 — iodates, ii, 68.
 — iodotetrachloride, ii, 68.
 — lead haloïds, ii, 524.
 — magnesium sulphate, crystallography of, TRANS., 347.
 — manganous sulphate, crystallography of, TRANS., 373.
 — nickelous sulphate, crystallography of, TRANS., 382.
 — — permanganate, ii, 324.
 — salts, preparation of, ii, 321, 414.
 — — pure, preparation of, ii, 521.
 — silver iodide, ii, 69.
 — spectroscopic estimation of, ii, 240.
 — telluribromide, ii, 457.
 — tellurichloride, ii, 457.
 — telluriiodide, ii, 457.
 — trihaloïds, ii, 67.
 — zinc sulphate, crystallography of, TRANS., 359.
 Ruthenium chloride, ammoniacal derivatives of, ii, 172.
 — fused, physical properties of, ii, 285.
 Rutile, artificial production of, ii, 173.
 Rye-flour, detection of wheat flour in, ii, 520.

S.

- "Saccharin," detection of, ii, 606.
 — detection of, in beer, ii, 504.
 Saccharose, dextrose, and levulose, analysis of a mixture of, ii, 99.

- Safranine, action of formaldehyde on, i, 573.
 Safranines, relation of, to indulines, i, 613.
 Safrole, thermochemistry of, ii, 154.
 Salicyladehyde, condensation of, with β -benzoylphenylhydrazine, i, 86.
 — detection of free salicylic acid in, ii, 503.
 Salicylamidoxime, dinitro-, TRANS., 1352.
 — nitro-, TRANS., 1352.
 Salicylanilide, bromo-, i, 211.
 Salicylic acid, amido-, i, 567.
 — detection of, ii, 503, 606.
 — dibromo-, i, 66.
 — dinitrodibromo-, i, 514.
 — estimation of, in presence of phenols, ii, 440.
 — free, detection of, in salicyl-aldehyde and methylsalicylic acid, ii, 503.
 Salicylide, i, 165.
 Salicylonitrile, dinitro-, i, 469; TRANS., 1351.
 — nitro-, i, 469; TRANS., 1351.
 — preparation and nitration of, TRANS., 1350.
 Saline hydrates and analogous compounds, dissociation of, ii, 364.
 Salt, crude, and brines, analysis of, ii, 391.
 — double, and its components, solution isotherms of, ii, 260.
 — solutions, aqueous, diffusion in, ii, 265.
 — aqueous, hydrolysis in, ii, 448.
 — equilibrium in, ii, 363.
 — labile conditions of equilibrium in, ii, 447.
 — rise of, in bibulous paper, ii, 109.
 Salts, acid, electrolytic dissociation of, ii, 365.
 — determination of the electrolytic dissociation of, ii, 364.
 — diffusion in aqueous solutions of mixed, ii, 565.
 — dissociation of, into their ions by water of crystallisation, ii, 265.
 — dissociation ratio of, ii, 565.
 — double, dissociation of, in solution, ii, 110.
 — existence of, in solution, ii, 450.
 — number of saturated solutions of, ii, 449.
 — ethereal, behaviour of, at high temperatures, i, 512.
 — influence of the concentration of the ions on the intensity of colour of solutions of, in water, ii, 203.
 — "insoluble," solubility of, ii, 519.
 Salts, soluble in water, determination of the specific gravity of, ii, 363.
 — vapour pressure of aqueo-alcoholic solutions of, ii, 154.
 Samarium, fractionation of, ii, 323.
 — simple nature of, ii, 526.
 — spectrum of, ii, 526.
 Sand, estimation of, in soils, ii, 97.
 Sandmeyer's reaction, i, 150; PROC., 1892, 199.
 Sanguinarine, i, 490.
Santalum prasi, crystalline substance from, i, 666.
 α -Santigendilactone, i, 664.
 Santogenen \acute{e} , i, 111.
 Santones, action of hydrochloric acid on the, i, 425.
 Santonin, i, 111, 112.
 — action of phosphorus pentachloride on, i, 425.
 — bromo-, i, 112.
 — constitution of, i, 364, 664.
 — derivatives of, i, 425.
 — fumaroid and maleinoid structure of some derivatives of, i, 425.
 — new isomeride of, i, 526.
 Santoninoxime, i, 363.
 — and its acetyl and benzyl derivatives, i, 664.
 Santoninoximic acid, i, 363.
 Santonins, reduction products of, i, 110.
 Santonone, i, 110.
 Santonic acid, i, 110.
 — acids, oxidation of, i, 665.
 Santonous acid, new isomeride of, i, 526.
 Saponins, i, 424.
 Sarcosolactic acid obtained by the fermentation of inactive lactic acid, TRANS., 1028.
 Sausages, detection of cochineal in, ii, 56.
 Scammonic acid, i, 423.
 Scammonin, i, 423.
 Scammonolic acid, i, 424.
 Scolezite from Brazil, ii, 423.
 Scoparin and its derivatives, i, 601.
 Scopoline platinochloride, crystalline form of, i, 739.
Scorzonera hispanica, isolation of coniferin from, 110.
 Sealing wax, analysis of, ii, 148.
 Secretion in the small intestine, ii, 582.
 Seeds, leguminous, carbohydrates in, ii, 139.
 Seleniobromides, ii, 318.
 Selenium, absorption of hydrogen selenide by, at a high temperature, ii, 457.
 — estimation of, ii, 318.
 Selenium-compounds, ii, 318.

- Semidines, ortho- and para-, i, 330.
- Senecio Kamperii*, unsaturated fatty acid from, i, 189.
- Senecioic acid, i, 189.
- Separations, quantitative, in presence of hydroxylamine, ii, 500.
- Serpentine, constitution of, ii, 78.
- Serum of blood and lymph, diastatic action of, ii, 333.
- of peptonised animals, gaseous tension in, ii, 131.
- Sesame oil, Baudoin's test for, ii, 197.
- Sesquiterpenes, i, 101.
- Siarenotannol, i, 666.
- Siarenotannyllic benzoate, i, 666.
- Silica, estimation of, in clay, ii, 300.
- reduction of, by carbon, ii, 532.
- volatilisation of, ii, 164, 460, 532.
- Silicates, aromatic, action of phosphorus oxychloride on, i, 74.
- estimation of alkalis in, ii, 436.
- estimation of, by Deville's method, ii, 491.
- ethereal, catalytic action of aluminium chloride on, i, 62.
- Silicon, action of, on gold, silver, platinum, and mercury, ii, 474.
- chloride, preparation of, ii, 10.
- estimation of, in aluminium, ii, 48.
- estimation of, in pig iron, ii, 435.
- new modification of, ii, 372.
- tetrachloride, molecular weight of, in the liquid state, TRANS., 1099.
- volatilisation of, in the electric arc, ii, 508.
- Silk, estimation of, in fabrics, ii, 611.
- Silver acetylide, preparation of, i, 121.
- action of ammonia on, ii, 207.
- action of hydrochloric acid on, under pressure, ii, 168.
- action of silicon on, ii, 474.
- action of various solvents on, ii, 207.
- and the alkali metals, double haloids of, ii, 69.
- behaviour of, in alcohol at the critical temperature, ii, 259.
- chloracetate, conditions affecting the decomposition of, ii, 266.
- chloride, ii, 208.
- — bromide, and iodide, solubilities of, ii, 520.
- — dry, action of light on, ii, 462.
- diazobenzene, i, 200.
- electrolytic estimation of, ii, 94.
- electrolytic separation of, from copper, ii, 305.
- electrolytic separation of, from lead, ii, 496.
- glycerate, TRANS., 309.
- Silver haloids, disruption of, by mechanical force, ii, 69.
- — hemisulphate, ii, 115.
- — nitrate, action of dry hydrogen chloride on, ii, 462.
- — action of hydrogen arsenide, antimonide, and phosphide on, ii, 206.
- — electrolysis of, in a vacuum, ii, 4.
- — oxide, action of, on magnesium nitrate, ii, 12.
- — — dehydration of, ii, 11.
- — refining of, ii, 17.
- — separation of, from bismuth, ii, 493.
- — separation of, from lead, ii, 492, 493.
- — solid colloidal, behaviour of, towards the electric current, ii, 314.
- — volatilisation of, in the electric arc, ii, 508.
- Silver-aluminium-bismuth alloys, ii, 416.
- Silver-aluminium-lead alloys, ii, 416.
- Silver-zinc-bismuth alloys, ii, 15.
- Silver-zinc-lead alloys, ii, 15.
- Slag, basic, estimation of calcium in, ii, 241.
- — estimation of phosphoric acid in, ii, 88, 238.
- — valuation of, ii, 344.
- Slags, crystallised, from Raibl, ii, 129.
- — estimation of phosphoric acid in, ii, 597.
- — estimation of phosphorus in, ii, 392.
- — estimation of sulphur in, ii, 89.
- Soap, estimation of soda in, ii, 191.
- — estimation of water and free fatty matter in, ii, 198.
- Soaps, estimation of resin in, ii, 609.
- Soda, estimation of, in soap, ii, 191.
- from the alkaline waters of Owen's Lake, ii, 18.
- — native, deposits of, near Laramie, Wyoming, ii, 535.
- Sodalite, synthesis of, ii, 19.
- Sodalite-group, ii, 421.
- Sodalite-syenite from Montana, ii, 538.
- Sodammonium, action of carbonic oxide on, ii, 520.
- — action of oxygen on, ii, 462.
- — molecular weight of, ii, 115.
- Sodium, action of alcohol on, at very low temperatures, ii, 113.
- — and potassium chlorides, rate of evaporation of solutions of, ii, 64.
- — — direct estimation of, by means of tartaric acid, ii, 598.
- — antimonites, ii, 171.
- — carbonate formation of, in nature, ii, 165.

- Sodium carbonyl, ii, 521.
- chloride, dissociation of, in presence of heated surfaces of porous clay, ii, 316.
 - — freezing point of dilute solutions of, ii, 263, 365, 447, 565.
 - — influence of, on the digestion and assimilation of proteid, ii, 579, 580.
 - dibromortho-xylenesulphonate, *PROC.*, 1892, 213.
 - ferrite, ii, 169.
 - flame, spectrum of, ii, 402.
 - glycerate, active and inactive, *TRANS.*, 302.
 - hydroxide, action of sulphuric acid on, at very low temperatures, ii, 112.
 - — hydrates of, *TRANS.*, 890.
 - infra-red emission spectrum of, ii, 58.
 - iodotetrachloride, ii, 68.
 - metallic, titration of acids with, ii, 550.
 - molybdoarsenates, ii, 282.
 - nitrate and ammonium sulphate, relative value of, as manures for barley and oats, ii, 593.
 - — estimation of nitrogen in, ii, 87.
 - nitrite, estimation of nitrous acid in, ii, 43.
 - oxalate, action of, on voluntary muscle, ii, 480.
 - perchromate, ii, 471.
 - peroxide, use of, in analysis, ii, 387; *TRANS.*, 1079.
 - platinoeyanide, i, 541.
 - propoxide, action of iodine on, i, 383, 682.
 - separation of magnesium from, ii, 47.
 - silicates, solutions of, ii, 166.
 - sulphate, magnetic rotation of solutions of, *TRANS.*, 64.
 - sulphide, sulphite, and thiosulphate, estimation of, in the glycerol from soap works, ii, 348.
 - thiosulphate, action of potassium permanganate on, ii, 164.
 - titanites, crystallised, ii, 125.
- Soil and nitrification, ii, 486.
- effect of sterilisation on the fixation of nitrogen by, ii, 291.
 - estimation of ferric oxide in, ii, 243.
 - influence of the distribution of manures in the, on their utilisation, ii, 141.
 - power of propagation of leguminous bacteria in a, ii, 32.
 - reversion of soluble calcium phosphate in, ii, 431.
- Soils, ammoniacal fermentation in, ii, 291.
- arable, drainage water from, ii, 338.
 - estimation of clay and sand in, ii, 97.
 - estimation of nitrogen in, ii, 601.
 - estimation of nitrogen in, by Kjeldahl's method, ii, 43.
 - estimation of phosphorus in, ii, 489.
 - influence on vegetation of the pressure of carbonic anhydride in the air of, ii, 341.
 - organic constituents of, ii, 341.
- Solid, dependence of the solubility of, on its melting point, ii, 366.
- Solid-solutions, a case of, ii, 73.
- Solubility, influence of hydration on, ii, 509.
- of a solid, dependence of, on its melting point, ii, 366.
 - of "insoluble" salts, ii, 519.
- Solution, capillary separation of substances in, *PROC.*, 1893, 123.
- dissociation theory of, ii, 565.
 - existence of double salts in, ii, 450.
 - isotherms of a double salt and its components, ii, 260.
- Solutions, acid or saline, relations between the specific gravity of, and the molecular weight of the dissolved substance, ii, 7.
- application of Raoult's law at the boiling points of, ii, 406.
 - aqueous, relations between the boiling points and osmotic pressures of, ii, 260.
 - — salt, diffusion in, ii, 265.
 - — temperature of maximum density of, ii, 60.
 - — volume changes in, ii, 477.
 - deviations from gaseous laws in, ii, 265.
 - dilute, of electrolytes, diffusion of, ii, 155.
 - — of sodium chloride, freezing point of, ii, 447, 565.
 - influence of gravity on the concentration of, ii, 315.
 - internal pressure in, ii, 447.
 - nature of, ii, 315.
 - new means of investigating the nature of certain, ii, 566.
 - non-electrolytic dissociation in, ii, 509.
 - of mixed salts, diffusion in, ii, 565.
 - of sodium and potassium chlorides, rate of evaporation of, ii, 64.
 - of sulphuric acid, freezing points of, ii, 262.
 - rotatory power of, ii, 106.

- Solutions, salt, hydrolysis in aqueous, ii, 448.
- labile conditions of equilibrium in, ii, 447.
 - rise of, in bibulous paper, ii, 109.
 - thermodynamical problems on conditions of equilibrium in, ii, 363.
 - saturated, of a double salt, the number of, ii, 449.
 - solid, a case of, ii, 73.
 - strong, properties of, TRANS., 998.
 - supersaturated, formation of, ii, 509.
 - the hydrate theory of, TRANS., 141.
 - very dilute, freezing points of, ii, 263, 365, 366.
 - weak, cryoscopic behaviour, of, ii, 110.
- Solvents, homogeneous mixed, elevation of boiling points of, ii, 260.
- melting points of, as the inferior limit of solubilities, ii, 111.
 - organic, influence of, on rotatory power, ii, 562.
 - participation of, in chemical reactions, ii, 367.
- Sparteine, derivatives of, i, 232.
- Specific gravities of the elements in the periodic system, ii, 513.
- gravity apparatus, ii, 264.
 - of acid or saline solutions and the molecular weight of the dissolved substance, relations between, ii, 7.
 - of ice, ii, 7.
 - of liquids, determination of, ii, 264.
 - of salts soluble in water, determination of, ii, 363.
- Specific heat of boron, ii, 404.
- of carbonic anhydride, ii, 5.
 - of erythritol and mannitol, ii, 258.
 - of liquid ammonia, ii, 258.
 - of the atoms, ii, 59.
 - of water, ii, 443.
- Specific inductive capacities and refraction constants, ii, 505.
- rotation of active acids, influence of metals on, TRANS., 296.
 - volumes of certain paraffins and paraffin derivatives, TRANS., 273.
 - of sulphur, ii, 8.
- Spectra, absorption, of chromium compounds, ii, 313.
- of copper salts in solution, ii, 149.
 - flame-, of some metals, ii, 402.
 - of aluminium, indium, and thallium, ii, 313.
 - of easily volatile metals, method of observing, TRANS., 138.
- Spectra of the flames of some metallic compounds, ii, 401.
- spark-, of the elements, physical character of the lines of, ii, 2.
 - ultra-red, of the alkalis, ii, 58, 313.
- Spectrum, absorption, of liquid oxygen, ii, 353.
- analysis, quantitative, ii, 295.
 - the oxy-coal-gas flame for, ii, 594.
 - of liquid oxygen, ii, 201.
 - of samarium, ii, 526.
 - of thallium, ii, 525.
- Sperm oil, analysis, of, ii, 310.
- Sphene, artificial production of, ii, 129.
- Spherulites in acid eruptive rocks, constitution of, ii, 287.
- Spiegel, siliceous, analysis of, ii, 304.
- Spinal cord, proteids of the, ii, 479.
- Spleen, proteids of the, ii, 425.
- Spring, iodine, in Austrian Silesia, ii, 579.
- Spruce oil, 659.
- Stachydrine, i, 447, 679.
- Stachyose, estimation of, in the tubers of *Stachys tuberosa*, ii, 53.
- inversion of, i, 249.
- Stachys tuberosa*, composition and nutritive value of the tubers of, ii, 225.
- organic bases in the tubers of, i, 679.
- Standardisation of acid and alkaline solutions, ii, 232.
- Stannic acid, combination of oxalic acid with, i, 625.
- Stannic iodide, solubility of, in methylenic iodide, ii, 378.
- Stannite from the Black Hills, Dakota, ii, 324.
- Starch, action of hydrogen peroxide on, i, 384.
- amount of, in different varieties of potatoes, ii, 430.
 - changes of, in mashing, i, 684.
 - combination of iodine with, i, 683.
 - conversion of, into sugar by means of blood serum, i, 187.
 - estimation of, ii, 249.
 - formation of dextrose from, i, 4.
 - hexanitro-, i, 6.
 - higher nitro-derivatives of, i, 6.
 - migration of the, in the tubers of potatoes, ii, 485.
 - non-crystallisable products of the action of diastase on, i, 127.
 - of leaves, TRANS., 604.
 - of the leaf, estimation of, TRANS., 622.
 - pentanitro-, i, 6.

Starch, products of the transformation of, by leaf-diastase, TRANS., 634.
 — soluble, action of leaf-diastase, on, TRANS., 651.
 — tetranitro-, i, 6.
 Starvation, physiology of, ii, 477.
 Stas Memorial Lecture, TRANS., 1.
 Steam, electrolysis of, ii, 515.
 Stearic acid hydrazide, i, 332.
 — — solubility of the lead salt of, in ether, i, 548.
 Steel, analysis of, ii, 499.
 — estimation of aluminium in, ii, 49, 243.
 — estimation of carbon in, ii, 45, 491.
 — estimation of chromium in, ii, 554.
 — estimation of phosphorus in, ii, 43, 44, 235, 392, 553, 596.
 — passive state of, ii, 16.
Stellaria graminea, analysis of, ii, 593.
 Stereochemical notation, i, 195.
 Stereochemistry, ii, 255.
 — of nitrogen, ii, 157.
 — of unsymmetrical hydrazones, i, 207.
 — or motochemistry?, ii, 513.
 Stereoisomerides, determination of the number of, i, 681.
 Stereoisomerism of nitrogen compounds, TRANS., 1069.
 Sterilisation of urine by light, cause of, TRANS., 1119.
 Stibiotantalite, TRANS., 1076.
 Stilbene, bromo-, i, 342.
 — conversion of derivatives of diphenyltrichlorethane into, i, 271.
 — dinitro-, i, 697.
 — formation of, i, 350.
 — orthodichloro-, i, 351.
 — dichloride, i, 351.
 — thionyl diamido-, i, 518.
 — trichloro-, i, 351.
 Stilbenedisulphonic acid, dinitroso-, salts of, i, 697.
 Stirrer for liquids, ii, 452.
 Stomach, absorption from, ii, 581.
 — bacteria of the, ii, 223.
 — estimation of hydrochloric acid in the contents of, ii, 86.
 — occurrence of hydrochloric acid in, ii, 540.
 Stomach-contents, occurrence of ammonia in, ii, 177.
 Strontium and barium bromides, separation of, by means of amyl alcohol, ii, 241.
 — and calcium nitrates, separation of, by means of amyl alcohol, ii, 241.
 — arsenates, ii, 274.
 — barium and calcium, separation of, ii, 436.
 — bromate, decomposition of, by heat, ii, 11.

Strontium-bromide, accumulation of, in the organism, ii, 217.
 — carbonate, solubility of, ii, 520.
 — detection of, in presence of calcium, ii, 47, 92.
 — flame-spectrum of, ii, 402.
 — fluoride, ii, 414.
 — glycerate, active and inactive, TRANS., 299.
 — iodide, action of, on the circulation, ii, 222.
 — oxide, action of a high temperature on, ii, 167.
 — salts, elimination of barium from ii, 209.
 — separation of, from calcium, ii, 301.
 — sulphate, solubility of, ii, 520.
 — sulphite, ii, 456.
 — zincoxide, ii, 118.
 Structure, change of colour as indicative of change of, PROC., 1893, 55.
 — optical properties as indicative of, PROC., 1893, 57.
 Strychnine lævo-phenyldibromopropionate, i, 94.
 — nitrate, the hydrochloric acid test for, ii, 397.
 — oxidation of, i, 287.
 — solutions, rotatory power of, ii, 106.
 Suberene, i, 13.
 Suberone, constitution of, i, 557.
 Succinamide, oxy-, i, 632.
 Succindi- β -naphthalide, i, 99.
 Succinic acid, bromo-, action of water on, i, 192.
 — — chloro-, an active, i, 250.
 — — dibromo-, action of aniline on, i, 564.
 — — — action of paratoluidine on, i, 565.
 — — estimation of, ii, 557.
 — — estimation of, in alcoholic liquids, i, 10.
 — — mesodiamido-, i, 692.
 — — racemic diamido-, i, 693.
 — — solubility of, i, 10.
 — — sp. gr. of, i, 11.
 — acids, dibromo-, i, 142.
 — — isomeric diamido-, i, 692.
 — — substituted, anhydride formation in the case of, i, 693.
 — — anhydride, allo- $\alpha\beta$ -dichloro-, i, 143.
 — — chloride, $\alpha\beta$ -dichloro-, i, 143.
 Succinimide, bromo-, i, 310.
 — bromyl-, i, 305.
 — chloryl-, i, 192.
 β -Succinylphenylhydrazide, i, 370.
 Sugar, cane-, action of boiling water on, i, 64.
 — — benzoate from, i, 116.
 — — compounds of, with calcium oxide, i, 451.

- Sugar, cane-, "spontaneous" inversion of, i, 547.
- conversion of starch into, by means of blood serum, i, 187.
 - detection of, in urine, ii, 349, 610
 - detection of small quantities of, in urine, ii, 349.
 - effect of phosphate manuring on the amount of, in beet, ii, 228.
 - estimation of, ii, 52, 100, 248, 398, 555, 601.
 - estimation of, in blood, ii, 398.
 - estimation of, in cocoa preparations, ii, 100.
 - estimation of, in tomatoes, ii, 555.
 - estimation of, in wine, ii, 52.
 - formation of hydrocyanic acid by the action of nitric acid on, i, 617.
 - formation of, in the liver, ii, 25.
 - from pear pectose, i, 248.
 - grape-, estimation of, ii, 248.
 - in muscle, ii, 383.
 - influence of, on the constitution of milk fat, ii, 27.
 - inversion of, by feeble acids, ii, 62.
 - inversion, velocity of, in presence of acetic and lactic acids, ii, 112.
 - milk-, benzoate from, i, 186.
 - physiological action of, ii, 584.
 - rate of inversion of, in aqueo-alcoholic solution, ii, 160.
 - use of metaphosphoric acid to remove proteids in estimating, in milk, ii, 248.
- Sugars, birotation and hydrazone formation of some, i, 125.
- characterisation of, i, 4.
 - estimation of, by means of Fehling's solution, ii, 601.
 - estimation of inorganic constituents in, ii, 51.
 - of the leaf, TRANS., 659.
 - physiological action of, ii, 584, 585.
 - rotatory power of, i, 186.
 - synthesis of, i, 125.
- Sulphamide, ii, 268.
- Sulphanilic acid azoquinol, i, 571.
- Sulphates, action of ammonia on, ii, 118.
- action of sulphur and water on, ii, 205.
 - volumetric estimation of, in potable waters, ii, 245.
 - volumetric estimation of sulphuric acid in, ii, 188, 240.
- Sulphides, estimation of sulphur in, ii, 186.
- mineral, artificial production of, ii, 214.
- Sulphimide, ii, 269.
- Sulphinic acids, nitro-, i, 168.
- Sulphinolactones, i, 458.
- Sulphites, metallic basic, ii, 455.
- o*-Sulphobenzoic acid, monammonium salt of, i, 715.
- Sulphoborite, ii, 325.
- Sulphocamphylic acid, i, 363; PROC., 1893, 109.
- γ -Sulphonedibutyric acid, i, 9.
- Sulphonefluoresceïn, i, 94.
- Sulphonephthaleïns, i, 94.
- Sulphones, hydrolysis of, i, 458.
- Sulphonesulphinic acids, i, 458.
- Sulphonic acids, aromatic, constitution of the iodides of, i, 269.
- chlorides, action of heat on, PROC., 1893, 130.
- Sulphur, action of, on charcoal, ii, 571.
- action of, on salts of polybasic acids in presence of water, ii, 205.
 - chloride, molecular weight of, in the liquid state, TRANS., 1099.
 - Eschka's process for the estimation of, ii, 239.
 - estimation of, ii, 89, 186, 187, 189, 239, 389, 433, 551; TRANS., 1080.
 - estimation of, by fusion, influence of the sulphur contained in coal gas on, ii, 239.
 - estimation of, in coal, ii, 89, 187.
 - estimation of, in iron, ii, 389.
 - estimation of, in minerals by aid of sodium peroxide, TRANS., 1080.
 - estimation of, in organic liquids, ii, 433.
 - estimation of, in organic substances, ii, 187, 433.
 - estimation of, in roasted pyrites, ii, 197.
 - estimation of, in slags, ii, 89.
 - estimation of, in sulphides, ii, 186.
 - methods of estimating, ii, 551.
 - microchemical detection of, ii, 295.
 - molecular weight of, in solution, ii, 511.
 - plastic, from sulphur vapour, ii, 455.
 - specific volume of, ii, 8.
- Sulphur-compounds, boiling and melting points of, ii, 445.
- influence of, on metabolism, ii, 288.
 - organic, i, 35.
- Sulphuric acid, action of, on alkalis at very low temperatures, ii, 112.
- amide and imide of, ii, 268.
 - and its aqueous solutions, magnetic rotation of, TRANS., 57, 59.
 - carbonic acid, calcium, and magnesium, distribution of acids and bases in a solution containing, TRANS., 696.
 - depression of the freezing point of acetic acid by, TRANS., 1026.

Sulphuric acid, estimation of, ii, 89, 145, 188, 239, 240.
 ——— freezing points of solutions of, ii, 262.
 ——— gravimetric estimation of, ii, 145.
 ——— molecular volume of, in solution, TRANS., 102.
 ——— poisoning, ii, 335.
 ——— production of hydrogen peroxide in the electrolysis of, ii, 108.
 ——— refractive indices and magnetic rotations of solutions of, TRANS., 99.
 ——— solutions, density and composition of, ii, 61, 155.
 ——— volumetric estimation of, in alkali sulphates, ii, 89.
 ——— volumetric estimation of, in sulphates, ii, 89, 188, 240.
 Sulphuric anhydride and arsenious anhydride, compounds of, ii, 66, 459.
 Sulphurous acid, estimation of, in wine, ii, 189.
 ——— anhydride, absorption of, by caoutchouc, ii, 564.
 ——— action of, on oxy-salts, ii, 115.
 ——— conditions of the absorption of, by calcium oxide, TRANS., 829.
 ——— density, &c., of, ii, 516.
 Sulphuryl chloride, molecular weight of, in the liquid state, TRANS., 1099.
 ——— holoxide, ii, 413.
 ——— peroxide, ii, 413.
 Sundite from Oruro, Bolivia, ii, 382.
 Sunflower cake, feeding experiments on cows with, ii, 328.
 Superphosphates, soluble phosphoric acid in, ii, 549.
 Surface tensions of liquids and their chemical constitution, relation between, ii, 8.
 Surinamine, i, 182.
 Svabite, ii, 420.
 Synanthrin, i, 618.
 Synovin and mucin, ii, 330.
 Synthesis, chemical, general method of, ii, 112, 451.
 Syntheses with aluminium chloride, i, 718.

T.

Tagetes glandulifera, flowers of, i, 623.
 Talc, rose-coloured lime and alumina-bearing, ii, 538.
 Tanacetene, i, 107.
 Tanacetogendicarboxylic acid, i, 108.
 ——— anhydride, i, 108.
 Tanacetogenic acid, i, 107.
 Tanacetoketocarboxylic acid, i, 107.
 Tanacetone, i, 107.

Tanacetophorone, i, 108.
 Tanacetoxime, i, 107.
 ——— conversion of, into 1 : 3 : 4-cymidine, i, 78.
 Tanacetylamine, i, 107.
 Tanacetylic alcohol, i, 107.
 ——— chloride, i, 107.
 Tannin, estimation of, in wine, ii, 52, 311.
 ——— from chestnut bark, i, 343.
 Tannin-indigo, constitution of, i, 510.
 Tap for vacuum desiccators, ii, 453.
 Tar from the bark of *Populus tremula*, i, 454.
 Tartar emetic, stability of standard solutions of, ii, 600.
 Tartaric acid, detection and estimation of lead in, ii, 557, 599.
 ——— estimation of, in a mixture of calcium tartrate and malate, ii, 558.
 ——— formula of, i, 593.
 ——— ketonic compound from, i, 685.
 ——— molecular volumes and molecular rotations of ethereal salts of, TRANS., 527.
 ——— oxidation of, in presence of iron, PROC., 1893, 113.
 ——— rate of diffusion of dextro- and lævo-rotatory, ii, 316.
 Tartrates, action of sulphur and water on, ii, 205.
 Tartrylbenzalhydrazine, i, 731.
 Tartrylhydrazine, i, 731.
 Tea, estimation of caffeine (theine) in, ii, 352, 608.
 ——— influence of, on artificial digestion, ii, 540.
 Teeth, fluorine in, ii, 81.
 Tellurium, double haloïd compounds of, with potassium, cesium, and rubidium, ii, 457.
 ——— properties of, ii, 205.
 Temperatures, critical, new method of calculating, TRANS., 1107.
 ——— of liquids, ii, 111.
 ——— cryohydric, ii, 512.
 ——— low, effect of, on chemical action, ii, 112.
 ——— low, formation of nitro-derivatives at, i, 460.
 ——— of maximum density of aqueous solutions, ii, 60.
 ——— of reaction and heats of formation, relation between, ii, 152.
 Tennantite from Aspen, Colorado, ii, 75.
 Tensions of vapours, ii, 9.
 Teraerylic acid, constitution of, TRANS., 1330.
 Terbia, complex nature of, ii, 466.
 Terebenthene, action of acetic and formic acids on, i, 358.

- Terebenthenealdehyde, i, 361.
 Terephthalic acid, nitro-, electrolytic reduction of, i, 567.
 Terpene-derivatives, oxidation of, i, 596.
 Terpenes, *Proc.*, **1893**, 163.
 — aldehydes from, i, 360.
 — and allied compounds, *TRANS.*, 75.
 — and their derivatives, i, 277.
 — dextro-, in Russian turpentine, valency of, i, 358.
 — from resins, i, 100.
 — series, constitution of the members of, i, 276.
 — — orientation in the, i, 359.
 — — oxidation in the, i, 722.
 Terpenylic acid, constitution of, *TRANS.*, 1338.
 — — reduction of, *TRANS.*, 1343.
 Terphenylphenylurethane, i, 595.
 Terpinene, oxidation of, *TRANS.*, 294.
 Terpeneol, i, 595.
 — methyl ether, i, 359.
 — oxidation of, i, 596.
 Terpinol, oxidation of, *TRANS.*, 1329.
 Terpinolene, oxidation of, *TRANS.*, 295.
 Terpylonic acid, *TRANS.*, 1329.
 Tetrabenzoylpenterythritol, i, 617.
 Tetracalcium phosphate, formation and properties of, ii, 70.
 Tetracetamidotertiarybutylbenzene, i, 636.
 Tetracetylalabinonitrile, i, 294.
 Tetracetylthane, i, 631.
 Tetraglycerol, i, 617.
 Tetrahydrobenzene, i, 255.
 Δ^1 -Tetrahydrobenzoic acid, i, 34.
 Δ^2 -Tetrahydrobenzoic acid, i, 33.
 Tetrahydrocarbazole, preparation of, i, 717.
 Tetrahydrocarveol, i, 359.
 Tetrahydrocarvole, i, 359.
 Tetrahydromethylphenometadiazine, i, 531.
 Tetrahydro-2'-ethylquinazoline, i, 51.
 Tetrahydroisoquinoline, i, 227, 528.
 — nitroso-, i, 528.
 — tetrahydroisoquinolinedithiocarbamate, i, 529.
 Tetrahydroisoquinolylcarbamide, i, 529.
 Tetrahydronaphthalene, derivatives of, i, 591.
 Tetrahydronaphthylene chlorhydrin, i, 591.
 — glycol, i, 591.
 — metaglycol, i, 592.
 — oxide, i, 591.
 Tetrahydroparatoluic acid, i, 713.
 Tetrahydropheno-2'-methyl-4'-phenylmetadiazine, i, 49.
 1 : 3 : 5-Tetrahydrophenyldimethylpyrazole, i, 178.
 Tetrahydro,2'-phenylquinazoline, i, 50.
 Tetrahydrophthalazine, i, 733.
 Tetrahydroxyanthraquinolinequinone, i, 671.
 Tetrahydroxydibenzylidicarboxylic acid, i, 588.
 Tetrahydroxydinaphthylmethane, i, 222.
 Tetrahydro-xylene, i, 525.
 Tetrahydroxyoctolactone, i, 12.
 Tetraketones, aromatic, i, 169.
 Tetramethoxydihydrodiphthalyldiimide, i, 372.
 Tetramethoxydiphthalyl, i, 588.
 Tetramethoxydiphthalylic dibromide, i, 588.
 Tetramethoxydiphthalylimide, i, 588.
 Tetramethoxydiphthallylactonic acid, i, 588.
 Tetramethoxyhydrodiphthallylactonic acid, i, 588.
 Tetramethoxyphenyldipiazine, *TRANS.*, 1304.
 Tetramethylamidazoxybenzene, i, 509.
 Tetramethyldiamidobenzophenone, thermochemistry of, ii, 6.
 Tetramethyldiamidodiphenylmethane, thermochemistry of, ii, 6.
 Tetramethyldiamidothiobenzophenone, thermochemistry of, ii, 6.
 Tetramethyldihydroxyheptamethylene, *TRANS.*, 117.
 Tetramethylenecarboxylic acid, tribromo-, i, 694.
 Tetramethylene-derivatives, i, 693.
 Tetramethylenediamine, action of nitrous acid on, i, 453.
 Tetramethylenedicarboxyanil, i, 694.
 Tetramethylenedicarboxylic acid, i, 693.
 — — dibromo-, i, 694.
 Tetramethylenetetracarboxylic acid, i, 693.
 Tetramethylethylene, hydration of, i, 61.
 Tetramethylhomoidamine thiosulphate, i, 77.
 Tetramethyloxetone, i, 691.
 Tetramethyloxetonecarboxylic acid, i, 690.
 Tetramethylphenyltriamidotriphenylmethane, i, 515.
 α -Tetramethylpiperazine, i, 374.
 β -Tetramethylpiperazine, i, 374.
 Tetramethylsuccinic acid, i, 394.
 Tetramethyltolyltriamidotriphenylmethane, i, 516.
 Tetramolybdoperiodic acid, salts of, ii, 123.
 Tetraphenyldipiazine, *TRANS.*, 1299.
 Tetraphenylenefurfuran, *TRANS.*, 772.
 Tetrasalicylide, i, 166.
 Tetrazole-derivatives from diazotetrazotic acid, i, 440.
 Tetrazylhydrazine, i, 441.

- Tetric acid, derivatives of, i, 690.
 Tetrolie acid diiodide, i, 397.
 Thallium, atomic weight of, ii, 322.
 — flame-spectrum of, ii, 402.
 — method of obtaining a persistent spectrum of, TRANS., 139.
 — silver nitrate, use of, for separating minerals, ii, 294.
 — spectrum of, ii, 313, 402, 525; TRANS., 139.
 — sulphite, ii, 278, 456.
 — volumetric estimation of, ii, 92.
 Thallochlore, i, 41.
Thamnia vermicularis, acid from, i, 277.
 Thamnic acid, i, 727.
 Theine and caffeine, identity of, TRANS., 195.
 — estimation of, in tea, ii, 352, 608.
 Theobromine and caffeine, separation of, ii, 608.
 — estimation of, in cacao beans, ii, 198.
 — thermochemistry of, ii, 362.
 Thermal expansion of certain paraffins and paraffin derivatives, TRANS., 273.
 — of liquids, determination of, TRANS., 262.
 — value of the three acid functions of phosphoric acid, ii, 60.
 Thermochemistry of carbon compounds of mixed functions, ii, 6.
 — of chloracetic acid, i, 624.
 — of α -dibromopropionic acid, ii, 358.
 — of β -dibromopropionic acid, i, 625.
 — of indigotin derivatives, i, 649.
 — of isomeric allyl and propenyl derivatives, ii, 153.
 — of levulinic, pyrotartaric, and racemic acids, ii, 109.
 — of monobromanilines, i, 22.
 — of polybasic ureides, ii, 360.
 — of substituted benzenoid hydrocarbons, i, 562.
 — of the ions, ii, 357.
 — of ureides, ii, 358.
 — of uric acid, ii, 360.
 Thermodynamical problems on conditions of equilibrium in salt solutions, ii, 363.
 Thermoelectric phenomena between two electrolytes, ii, 202.
 Thermometer, air, for laboratory use, ii, 357.
 — mercurial, for temperatures up to 550°, ii, 443.
 Thiazine, i, 44.
 Thiazolines, i, 532.
 Thiazone, i, 44.
 Thienylindole, i, 168.
 Thiocarbamide, constitution of, i, 341.
 — thermochemistry of, ii, 359.
 — See also Thiourea.
 Thiocyanacetone, i, 64, 188.
 Thiocyanates, detection and estimation of, in ammonium sulphate, ii, 556.
 — of chromammonium compounds, i, 290.
 — reactions of ferric salts with, i, 122, 185, 289, 290.
 Thiocyanic, hydrocyanic, and hydrochloric acids, estimation of, ii, 503.
 Thiohydantoin, thermochemistry of, ii, 362.
 Thionuric acid, ii, 361.
 Thionyl bromide, PROC., 1893, 10.
 — chloride, molecular weight of, in the liquid state, TRANS., 1099.
 — preparation of, i, 504.
 — chlorides, action of, on acid amides, i, 553.
 Thionylamines, i, 504.
 — of the aliphatic series, i, 504.
 — of the aromatic series, i, 515.
 — of unsaturated bases, i, 702.
 Thionyl-diethylhydrazone, i, 249.
 Thiophen of crystallisation, i, 406.
 Thiosemicarbazides, stereoisomeric, i, 26.
 Thiosulphates, normal metallic, ii, 458.
 Thiourea, action of α -bromopropionic acid on, TRANS., 818.
 — action of dichloroacetic acid on, TRANS., 816.
 — action of trichloroacetic acid on, TRANS., 818.
 — and some haloïd derivatives of fatty acids, action between, TRANS., 815.
 Thioureas, substituted, desulphurisation of, TRANS., 318.
 Thiovanadates, formation of, ii, 379.
 Thiuret, i, 575.
 Thorium and uranium dioxides, isomorphism of, ii, 378.
 — extraction of, ii, 532.
 — preparation of, in the electric furnace, ii, 473.
 — sulphur compounds of, ii, 574.
 Thrombosis, cardiac and pulmonary, ii, 541.
 Thuja, oil of, constituents of, i, 105.
 α -Thujaketonic acid, i, 106.
 β -Thujaketonic acid, i, 107.
 Thujaketonic acids, constitution of, i, 598.
 Thujone, i, 106.
 — action of bromine and of bleaching powder on, i, 598.
 Thujylamine, i, 106.
 Thymol, compound of, with aluminium chloride, i, 508.
 — dibromo-, derivatives of, i, 316.
 — in the ethereal oil of *Mosula Japonica*, ii, 181.
 — titanate, i, 257.
 Thyroid, proteïds of the, ii, 425.

- Uiconine, bromo- and dibromo-, i, 287.
 Tiglic acid, brom-additive products of,
 i, 135, 188, 455.
 — — — constitution of, i, 141.
 — — — dibromide, i, 136.
 — — — index to the literature of,
 i, 10.
 — — — preparation of, i, 135.
 Tin and gold, compounds of, ii, 74.
 — — — detection of, ii, 192.
 — — — electrolytic estimation of, ii, 94.
 — — — estimation of, in alloys, ii, 95.
 — — — lead, antimony, and copper, separation of, ii, 95.
 — — — ore, assay of, ii, 501.
 — — — products of the action of nitric acid on, TRANS., 845.
 — — — separation of lead from, ii, 437.
 — — — slags, decomposition of, by the fluoride method, ii, 305.
 — — — sulphite ii, 456.
 — — — volatilisation of, in the electric arc, ii, 508.
 Tin-aluminium-bismuth alloys, ii, 415.
 Tin-copper-antimony alloys, analysis of, ii, 242.
 Tin-iron alloys, ii, 211.
 Tin-lead-aluminium alloys, ii, 415.
 Tin-zinc-bismuth alloys, ii, 15.
 Tin-zinc-lead alloys, ii, 15.
 Tissues, microchemical localisation of phosphorus in the, ii, 135.
 Titanic acid, action of a high temperature on, ii, 167.
 — — — combination of oxalic acid with, i, 625.
 Titaniferous iron ore from the Breitfirst, ii, 382.
 Titanium chloride, m. p. of, ii, 357.
 — — — specific gravity of, ii, 379.
 Titanium-compounds, i, 257.
 Titration apparatus with automatic zero adjustment, ii, 41.
 Tobacco, analysis of, ii, 504.
 — — — chemical changes in, during fermentation, ii, 592.
 — — — cured by the leaf-cure on wire and by the stalk process, analysis of, ii, 547.
 — — — plant, chemistry of the, ii, 38.
 — — — smoke, i, 226.
 — — — stalks, analysis of, when cut and after curing, ii, 592.
 Tolane, orthodichloro-, i, 351.
 — — — dichloride, i, 351.
 Tolazone, i, 733.
 — — — diamido-, i, 733.
 — — — dioxide, i, 733.
 Tolidine, thionyl-, i, 518.
 Toluamide, metanitro-, i, 212.
 Toluene, action of phenylthiocarbimide on, i, 154.
 — — — action of propyl bromide and aluminium chloride on, i, 562.
 — — — azimido-, oxidation of, i, 375.
 — — — 4 : 5-chloramido-, i, 340.
 — — — critical constants of, ii, 446.
 — — — dinitrochloro-, i, 15.
 — — — electrolytic reduction of, i, 566.
 — — — magnetic rotation of, ii, 442.
 — — — metachloro-, m. p. of, ii, 357.
 — — — nitration of, at low temperatures, i, 469.
 — — — ortho- meta- and para-bromo, m. p. of, ii, 357.
 — — — orthochloro-, m. p. of, ii, 357.
 — — — preparation of, i, 159.
 — — — orthiodoso-, i, 257.
 — — — orthiodoxy-, i, 257.
 — — — parachloro-, m. p. of, ii, 357.
 — — — paranitro-, action of alkalis on, i, 697.
 — — — pariodoso-, i, 256.
 — — — pariodoxy-, i, 257.
 — — — trichloro-, m. p. of, ii, 357.
 — — — α -trinitro-, preparation of, i, 14.
 Tolueneazocatechol, i, 410.
 o-Toluene- α -azonaphthalene, i, 276.
 o-Tolueneazo- β -naphthol, reduction of the acetyl-derivatives of, TRANS., 929.
 p-Tolueneazo- β -naphthol, reduction of the acetyl-derivatives of, TRANS., 925.
 m-Tolueneazophenetoil, reduction of, i, 330.
 o-Tolueneazophenetoil, reduction of, i, 330.
 p-Tolueneazophenetoil, reduction of, i, 330.
 Toluenedicarboxylic acid [1 : 2 : 6], i, 593.
 p-Toluenehydrazobenzoic acid, i, 47.
 o-Toluene- α -hydrazonaphthalene, i, 276.
 p-Tolueneorthazobenzoic acid, i, 47.
 Tolueneparasulphonic acid, 2 : 6-dinitro-, reduction of, i, 603.
 — — — nitramido-, i, 603.
 Toluenesulphonic acid, paranitro-, action of alkalis on, i, 697.
 Toluene-2-sulphonic acid, 4 : 5-chloronitro-, i, 339.
 — — — 4-nitro-, salts of, i, 270.
 Toluenesulphonic acids, amido-, affinity coefficients of, ii, 450.
 o-Toluic acid, action of phenylhydrazine on, PROC., 1892, 220.
 — — — dichloro-, i, 580.
 — — — dinitrochloro-, i, 581.
 — — — nitrochloro-, i, 581.
 — — — parachloro-, and its derivatives, i, 580.
 p-Toluic acid, 2 : 6-dinitro-, i, 604.
 — — — hydrobromide, i, 378.

- p*-Toluic acid, iodoso-, i, 581.
 ——— and iodoxy-derivatives of, i, 581.
 ——— nitro-, i, 581.
 ——— metiodo- and orthiodo-, i, 581.
 ——— acids, hydrogenised, i, 713.
 Toluidides which exist in two modifications, i, 511.
m-Toluidine, thionyl-, i, 516.
o-Toluidine, 4:5-chloronitro-, i, 580.
 ——— hydrogen malate, i, 265.
 ——— parachloro-, i, 699.
p-Toluidine hydrogen malate, i, 264.
 ——— oxidation of, TRANS., 1395.
 ——— thionyl-, and its derivatives, i, 516.
p-Toluidineazoquinol, i, 571.
o-Toluidines, metamidodialkylortho-, and their conversion into methylene-blue dyes, i, 75, 77.
 ——— paramidoalkyl-, i, 265.
 Toluidinesulphonic acids, alkyl-derivatives of, i, 584.
o-Toluenitrile, chloro-, i, 580.
 ——— nitrochloro-, i, 581.
 Toluquinoline chloral, i, 438.
 Toluquinone, action of hydrogen chloride on, i, 322.
 ——— chlorine and bromine additive products of, i, 320.
 Toluquinonediparatolylimide, TRANS., 1409.
 Toluquinoneditolylimide, amido-, TRANS., 1397, 1400, 1406.
 Toluquinoneparatolylimide, amido-, TRANS., 1401.
p-Toluy cyanide, i, 159.
 Toluylenediamine, chloro-, i, 15.
m-Toluylenediamine, thionyl-, i, 518.
 Toly di azoimides, i, 705.
 Toly isopropyl ketone, i, 162.
o-Toly iododichloride, i, 257.
p-Toly iododichloride, i, 256.
 ——— phenyl ketone, hydrazone of, i, 208.
o-Toly lacrylamide, i, 696.
p-Toly lacrylamide, i, 696.
 Tolyamidophenylamine, dinitro-, i, 15.
 Tolybenzimidophenyl ether, i, 409.
 Tolydiamidonaphthalene, i, 276.
o-Toly- $\alpha\gamma$ -diketo- $\beta\delta$ -dimethylpiperazines, isomeric, i, 51.
p-Tolyldimethylpyrimidine, i, 735.
p-Tolyldimethylquinolinethiocarbamide, i, 605.
o-Tolyfumaramide, i, 265.
p-Tolyfumaramide, i, 264.
o-Tolyhydrazine, bromination of, i, 705.
 ——— parabromo-, i, 705.
p-Tolyhydrazine, bromination of, i, 705.
 ——— bromo-, i, 705.
 1-*p*-Tolyindazole, i, 47.
 Tolyisopropylcarbinol, i, 162.
 Tolylllevulinic acid, β -thio-, i, 36.
p-Tolylmalamic acid, i, 264.
o-Tolylmalamide, i, 265.
p-Tolylmalamide, i, 264.
p-Tolylmalimide, i, 264.
 Tolylmethylamines, action of thionyl chloride on, i, 703.
 ——— thionyl-, i, 703.
 Tolyorthopiperazone, i, 705.
o- μ -Tolyloxazoline, i, 532.
p- μ -Tolyloxazoline, i, 533.
 μ -*o*-Tolylpenthiiazoline, i, 427.
 μ -*p*-Tolylpenthiiazoline, i, 427.
 Tolyphenylamine, dinitro-, i, 15.
 ——— nitro-, i, 340.
 Tolyphenylaminesulphonic acid, nitro-, salts of, i, 340.
o-Tolyphenylbenzenylamidine, i, 204.
 α -Tolyphenylformazyl methyl ketone, i, 159.
 1-*p*-Toly-5-phenylpyrazole-3-carboxylic acid, i, 610.
p- α -Tolyphenylthiosemicarbazide, i, 27.
o-Toly piperazine, diamido-, i, 54.
p-Toly piperazine, diamido-, i, 54.
p-Tolypropionic acid, β -thio-, i, 35.
p-Tolysulphoneanilide, i, 416.
p-Tolysulphone-ethylanilide, i, 416.
p-Tolysulphonemethylanilide, i, 416.
 Tolsulphoneoxysulphobenzide, i, 416.
o-Tolythiazoline, i, 534.
 Tomatoes, composition of the stems and leaves of, ii, 224.
 ——— estimation of sugar in, ii, 555.
 ——— presence of boron, copper, and lithium in, ii, 225.
 Tourmaline, formula of, ii, 422.
 Toxic action of aromatic compounds, influence of the carboxyl group on, ii, 178.
 ——— of expired air, ii, 223.
 Toxicity of certain mineral salts, ii, 179.
 Toxicological analysis, examination for metals in, ii, 598.
 Trehalase, i, 451.
 Trehalin, i, 496.
 Trehalose, occurrence of, in the fungi, ii, 337.
 Trehalum, i, 496.
 Train oil, recognition of paraffin and lubricating oil in the distillate of, under pressure, i, 493.
 Transfusion, some results of, ii, 22.
 Transparency, radiant, measurement of, ii, 401.
 Transudations, proteids in, ii, 334.
 Triacetyldibromogallie acid, i, 643.
 Triacetythane, unsymmetrical, i, 623.
 Triacetylpentaglycerol, i, 617.
 Triazoledicarboxylic acid [1:2:3], i, 375.

- Tribenzamide, i, 29.
 Tribenzenesulphonetrimethylenetri-
 imide, i, 714.
 Tribenzoyldibromogallic acid, i, 643.
 Tribenzoylpentaglycerol, i, 617.
 Tribenzylamine, preparation of, TRANS.,
 1311.
 Tricarbon-nuclei, action of zinc on
 bromo-derivatives of, i, 1.
 Trichosanthin, i, 42.
 Tricinamaltetraureide, i, 646.
 Tricinnamylamine, i, 570.
 Triethylamine, freezing points of aqueous
 solutions of, TRANS., 162.
 — hydrate of, TRANS., 162.
 — velocity of the reaction of, with
 ethylic iodide, ii, 510.
 Trihydriodocinchonidine, i, 231.
 Trihydroxyanthraquinolinequinone,
 i, 671.
 Trihydroxyaurin from catechol, i, 274.
 Trihydroxymethylisocarbostyryl, i, 367.
 Trihydroxymethylisocoumarin, i, 366.
 Trihydroxymethylisocoumarin, i, 367.
 β -Trihydroxynaphthoic acid, i, 475.
 Trimesic trihydrazine, i, 180.
 Trimethylamine, action of secondary
 caprylic iodide on, i, 7.
 — freezing point of aqueous solutions
 of, TRANS., 152.
 — hydrates of, TRANS., 154.
 Trimethylbenzimidazole [2 : 2' : 3'],
 i, 433.
 Trimethylcarbincarbinol, i, 543.
 Trimethylcarbinol, preparation of,
 i, 622.
 — specific volume and thermal ex-
 pansion of, TRANS., 278.
 Trimethylene chlorobromide, derivatives
 of, i, 8.
 — dichloro-, heat of combustion of,
 ii, 5.
 — heat developed by the union of
 bromine with, ii, 444.
 — heat of combustion of, ii, 444.
 Trimethylenediamine, β -chloro-, i, 31.
 Trimethylenediphtalimide, β -chloro-,
 i, 31.
 Trimethylenedisulphone, i, 459.
 Trimethyleneglycol diparatolyl ether,
 i, 9.
 Trimethylethylamine, i, 543.
 Trimethylethylene, i, 543.
 — action of nitrosyl chloride on,
 TRANS., 482.
 — behaviour of, with zinc chloride,
 i, 382.
 — formation of amylic salts by the
 action of acids on, i, 449.
 Trimethylethyl salts, i, 543.
 β -Trimethylethylidenelactic acid, action
 of sulphuric acid on, i, 71.
 Trimethylhydroxytetrahydronaphthyl-
 ammonium hydroxide, i, 592.
 Trimethylmethane, specific volume and
 thermal expansion of, TRANS., 276.
 Trimethylphloroglucinol, bromo-, i, 21.
 Trimethyltetrahydroquinoline, i, 227.
 Trimethyltrimethylenedisulphonesulph-
 ide, i, 684.
 Trimethylxanthine, derivatives of,
 i, 375.
 Trioxysparteine and its derivatives,
 i, 232.
 Triphenylacetone, preparation of,
 i, 589.
 Triphenylbenzene, i, 220.
 Triphenylcarbinol, preparation of,
 i, 589.
 Triphenyl- Δ_2 -ketotetrahydrobenzene
 [3 : 4 : 5], i, 419.
 Triphenylmethane, solubility of, in benz-
 ene, i, 273.
 Triphenylmethane-series, colouring mat-
 ters of the, i, 472.
 Triphenylloxazole, TRANS., 474.
 Triphenylphenol, i, 219.
 Triphenylpiperazine, i, 428.
 Triphenylpyrazolecarboxylic acid
 [1 : 4 : 5 : 3], i, 610.
 Triphenyltetrahydropyrazine, prepara-
 tion of, i, 428.
 Triphenylthiosemicarbazide, i, 29.
 Triphenylvinylalcohol, i, 718.
 Triphloroglucide, i, 718.
 Triphloroglucinol chloride, i, 718.
 Triphthalimidepropane, i, 31.
 Tripropylamidoacetic acid, i, 554.
 Triskaidecanic acid, amido-, and its de-
 rivatives, i, 552.
 α -Trithioaldehyde, behaviour of, in the
 organism, ii, 289.
 Tri-*p*-toluylene triamine, TRANS., 1395.
 Trona, artificial, ii, 577.
Tropaolum majus, sugars of, TRANS.,
 661.
 α -Tropine, i, 426.
 Tropine, formula of, i, 537.
 β -Truxillic acid, derivatives of, i, 418.
 γ -Truxillic acid, derivatives of, i, 419.
 δ -Truxillic acid, i, 58.
 Truxillic acids, constitution of, i, 418.
 Tuberculin, Koch's, constituents of,
 i, 234.
 Tunicin, i, 380, 497.
 Tungstates, preparation of, free from
 molybdenum, ii, 125.
 Tungsten, action of carbonyl chloride
 and of sulphur chloride on, ii, 574.
 — action of, on solutions of silver,
 gold, &c., ii, 170.
 — and iron, crystalline alloy of, ii, 170.
 — preparation of, in the electric fur-
 nace, ii, 471.

Tungstic anhydride, compounds of, with alkali oxalates, i, 457.
 Tungstous oxide, association of, with columbous oxide, ii, 531.
 Tungstyl chloride, action of gaseous ammonia on, ii, 531.
 Turacin, i, 184.
 Turacoporphyrin, i, 184.
 Turacoverdin, i, 184.
 Turkey red oil, i, 455.
 Turnip salad, analyses of, ii, 293.
 Turpentine, oil of, American, i, 594.
 ——— constitution of, i, 276.
 ——— French, action of picric acid on, TRANS., 1388.
 ——— oxidation of, TRANS., 1327.
 ——— Russian, valency of the dextro-terpenes in, i, 358.
 Turpethic acid, i, 424.
 Turpethin, i, 424.
 Turpethole, i, 424.
 Turpetholic acid, i, 424.

U.

Ulexine, i, 119.
 Undecaglyceryl, i, 544.
 Uramide, thermochemistry of, ii, 361.
 Uranium acetate, action of carbonic anhydride on, in sun-light, ii, 483.
 ——— colorimetric estimation of small quantities of, ii, 555.
 ——— dioxide and thorium dioxide, isomorphism of, ii, 378.
 ——— preparation and specific gravity of, ii, 378.
 ——— preparation of, ii, 283.
 ——— volatilisation of, in the electric arc, ii, 501.
 Uranyl sulphites, ii, 456.
 Urea, estimation of, ii, 146, 310, 560.
 ——— Hüfner's method of estimating, ii, 560.
 ——— in the blood of birds, ii, 581.
 Ureides, polybasic, thermochemistry of, ii, 360.
 ——— thermochemistry of, ii, 358, 360, 362.
 β -Ureidopropionic acid, i, 632.
 Urethane, derivatives of, i, 128.
 Uric acid, estimation of, ii, 558.
 ——— estimation of, in urine, ii, 101, 395.
 ——— formation of, ii, 428.
 ——— in the organism, ii, 384.
 ——— physiological action of, ii, 585.
 ——— solutions, behaviour of, when exposed to air, ii, 558.
 ——— thermochemistry of, ii, 362.

Urinary carbohydrates, relation of, to humous substance, ii, 82.
 ——— colouring matters, i, 539.
 ——— hæmatoporphyrin, ii, 480.
 Urine, action of light on, TRANS., 1112.
 ——— carbamic acid in, after ingestion of lime, ii, 333.
 ——— cause of the sterilisation of, by light, TRANS., 1119.
 ——— chromic acid as a reagent for albumin and bile pigments in, ii, 200.
 ——— conditions which favour the formation of hydrogen peroxide in, TRANS., 1115.
 ——— detection of albumin in, ii, 399, 610.
 ——— detection of bile pigments in, ii, 398.
 ——— detection of lead in, ii, 600.
 ——— detection of sugar in, ii, 349, 610.
 ——— estimation of diamines in, ii, 145.
 ——— estimation of mercury in, ii, 438.
 ——— estimation of nitrogen in, ii, 343.
 ——— estimation of uric acid in, ii, 101, 395.
 ——— fœtal, ii, 428.
 ——— formation of hydrogen peroxide in urine exposed to light, TRANS., 1110.
 ——— horse's, the phosphates of, ii, 30.
 ——— human, crystalline globulin occurring in, ii, 290.
 ——— in Bright's disease, transformation of the albumin of, ii, 30.
 ——— in cases of eczema, ptomaine from, i, 614.
 ——— in erysipelas and puerperal fever, ptomaines from, i, 183.
 ——— lactic acid in, ii, 136.
 ——— normal, the carbohydrates of, ii, 542.
 ——— pentoses in, ii, 100.
 ——— production of hydrogen sulphide and methyl mercaptan by a bacterium in, ii, 335.
 ——— source of error in the estimation of phosphoric acid in, ii, 99.
 ——— uroerythrin and hæmatoporphyrin in, ii, 178.
 ——— volumetric estimation of phenol in, ii, 100.
 Urobilin, ii, 428, 538.
 ——— pathological, i, 538.
 Urobilinogen, i, 538.
 Uroerythrin in urine, ii, 178.
 Urson and its derivatives, i, 601.

V.

Vacuum desiccators, tap for, ii, 453.
 Valeramide, isonitro-, i, 503.

Valeric acid, active, preparation of, from fusel oil, TRANS., 1130.
 ——— α -amidoxyl, i, 503.
 ——— β -bromo-, i, 689.
 ——— molecular weight of, in the liquid state, TRANS., 1103.
 ——— rotatory power of ethereal salts of, ii, 561.
 γ -Valerolactone- γ -acetic acid, i, 130.
 Valeronaphthalide, PROC., 1893, 8.
 ——— dinitro-, PROC., 1893, 9.
 Valeronitrile, α -amidoxyl, i, 503.
 Vanadates, thio-, formation of, ii, 379.
 Vanadic acid, estimation of, ii, 195.
 Vanadium alkali oxalates, i, 457.
 ——— extraction of, from its ores, ii, 17.
 ——— in a lignite from the Argentine Republic, ii, 128.
 ——— preparation of, in the electric furnace, ii, 471.
 Vanadyl trichloride, preparation of, ii, 17.
 Vanillideneorthamidobenzyl alcohol, i, 24.
 Van't Hoff-Wislicenus hypothesis, comparison of experimental results with the theoretical conclusions of the, i, 145.
 Vaporisation, speed of, of compounds in different atmospheres, ii, 564.
 Vapour density of halogen hydrides at low temperatures, ii, 65.
 ——— pressure of aqueous alcoholic solutions of salts, ii, 154.
 ——— pressures of certain ethereal salts, TRANS., 1191.
 ——— of fatty acids, ii, 446.
 ——— tension of mixtures of ether and water, ii, 264.
 ——— tensions of solutions of sulphur and phosphorus in carbon bisulphide, ii, 511.
 Vapours, tensions of, ii, 9.
 Varnish, linseed oil, testing, ii, 148.
 Vegetables, estimation of pentosans and pentoses in, ii, 53.
 Vegetation, influence on, of the pressure of carbonic anhydride in the air of soils, ii, 341.
 Velocity of chemical reactions, influence of dilution on, ii, 510.
 ——— of etherification, ii, 9.
 ——— of reaction between nitrites and hydroxylamine salts, ii, 160.
 ——— of sugar inversion in presence of acetic and lactic acids, ii, 112.
 Veratrine, crystallised, i, 490.
Vicia sativa, nitrogenous constituents of the seedlings of, ii, 85.
 α -Vinylbenzoic acid, octochloro-, i, 346.
 Volume changes in aqueous solutions, ii, 447.

Volumes, critical, ii, 63.
 ——— molecular, in corresponding states, ii, 63.
 ——— of dissolved alkali salts, ii, 264.
 Volumetric analyses, use of potassium hydrogen tartrate in, ii, 144.

W.

Walnewite, constitution of, ii, 78.
 Water and alcohol, distillation of mixtures of, ii, 347.
 ——— and ether, vapour tension of mixtures of, ii, 264.
 ——— apparatus for extracting the gases dissolved in, ii, 432.
 ——— as a catalyst, ii, 462.
 ——— bottle for taking samples of, at known depths, ii, 432.
 ——— composition of, ii, 453.
 ——— composition of, by volume, ii, 515.
 ——— depression of the freezing point of acetic acid by, TRANS., 1026.
 ——— depression of the freezing point of, by dissolved substances, TRANS., 1015.
 ——— drainage, from arable soils, ii, 338.
 ——— electrolytic dissociation of, ii, 364, 365, 448.
 ——— estimation of chlorine in, ii, 550.
 ——— estimation of hardness of, ii, 347.
 ——— gravimetric composition of, ii, 410.
 ——— influence of, in promoting chemical action, ii, 462; PROC., 1893, 129.
 ——— magnetic rotation of, ii, 412.
 ——— mineral, containing iodine, from Austrian Silesia, ii, 479.
 ——— of the Valle del Gallo, ii, 175.
 ——— molecular weight of, in the liquid state, TRANS., 1105.
 ——— of crystallisation, dissociation of salts into their ions by, ii, 265.
 ——— of the Black Sea, saline constituents of, ii, 326.
 ——— of the Eastern Mediterranean, ii, 216.
 ——— rain, bacillus in, ii, 83.
 ——— specific heat of, ii, 443.
 ——— spring, estimation of iron in, ii, 196.
 Waters, alkaline, of Owen's Lake, soda from, ii, 18.
 ——— mineral, composition of, TRANS., 696.

Waters, mineral, estimation of bromine in, ii, 595.
 — of Askern, in Yorkshire, *TRANS.*, 685.
 — of Barèges, sulphur compounds in, ii, 326.
 — potable, estimation of nitrites in, ii, 346.
 — volumetric estimation of sulphates in, ii, 245.
 — spring, zinc bearing, from Missouri, ii, 81.
 Wax, analysis of, by Hübl's method, ii, 198, 351, 397.
 — from chay root, *TRANS.*, 1166.
 — from kamala, *TRANS.*, 987.
 — of gum lac, i, 548.
 — qualitative and quantitative analysis of, ii, 351.
 Whartonite not a distinct species, ii, 535.
 Wheat, diastase of, i, 743.
 — experiments with, on the substitution of beryllium for magnesium, ii, 228.
 — flour, detection of, in rye flour, ii, 250.
 — occurrence of betaïne and choline in the sprouts of, i, 684.
 — pre-existence of gluten in, ii, 292.
 — proteïds of, i, 741.
 White lead, Dutch, supposed saponification of linseed oil by, *PROC.*, 1893, 122.
 — ground, analysis of, ii, 494.
 Wine, detection of adulteration in, ii, 501.
 — estimation of chlorine in, ii, 233.
 — estimation of citric acid in, ii, 54.
 — estimation of glycerol in, ii, 247, 248.
 — estimation of phosphoric acid in, ii, 389.
 — estimation of sugar and tannin in, ii, 52.
 — estimation of sulphurous acid in, ii, 189.
 — estimation of tannin in, ii, 52, 311.
 — estimation of the dry residue in, ii, 501.
 — presence of aldehyde sulphite in, ii, 189.
 Wines, succinic acid in, i, 10.
 Wong koudu, colouring principles of, *TRANS.*, 1184.
 Wood, fossil, fluorine in, ii, 76.
 Wood-gum, inversion of, i, 249.
 — parent substance of, i, 128.
 Wood-oil, constituents of, i, 558.
 Wool fat, detection of foreign fats in, ii, 351, 397.

Work, effect of, on the excretion of phosphoric acid, ii, 583.
 Worms, respiratory pigment in the blood of, i, 59.
 Wormseed, occurrence of betaïne and choline in, ii, 485.
 Worts, estimation of isomaltose in, ii, 601.
 Wounds, antiseptic action of, ii, 223.

X.

Xanthine, monosodium derivative of, i, 536.
 Xanthine-derivatives, behaviour of, with hydroxylamine and Fehling's solution, i, 535.
 — titration of, i, 535.
 Xanthogenamide, action of trimethylene chlorobromide on, i, 427.
 Xanthone-derivatives, i, 217.
 4 : 5-Xanthonedicarboxylic acid, i, 217.
 Xanthophene, *PROC.*, 1892, 192.
 Xanthydrol, i, 471.
 Xanthidryl ether, i, 472.
 Xenotime from El Pasco Co., Colorado, ii, 537.
 Xylan, parent substance of, i, 128.
 Xylene, tetriodo-, i, 407.
 o-Xylene, chloro-derivatives of, and their relations to the chlororthotoluic acids, i, 586.
 Xylenes, behaviour of, in the organism, ii, 178.
 — critical constants of, ii, 446.
 — magnetic rotation of, ii, 442.
 m-Xylenesulphonic acid, diiodo-, i, 407.
 — iodo-, i, 407.
 o-Xylenesulphonic acids, chlor-, i, 586.
 — isomeric change in, *PROC.*, 1892, 213.
 m-Xylenol, bromo-, *TRANS.*, 110.
 — nitro-, *TRANS.*, 105.
 m-Xylenolsulphonic acid, *TRANS.*, 110.
 p-Xylic acid, *TRANS.*, 90.
 p-Xylidine, i, 198.
 Xylidines, thionyl-, and their derivatives, i, 516.
 Xylidinic acid, *TRANS.*, 92.
 Xylocatechol, *TRANS.*, 108.
 Xylocatechyllic monomethylic ether, *TRANS.*, 107.
 Xylose, i, 248, 294.
 Xyloyl cyanide, i, 160.
 Xyloylformoxime, i, 160.
 m-Xylol propyl ketone, i, 162.
 — isopropyl ketone, i, 162.
 o-Xylol isopropyl ketone, i, 162.
 p-Xylol propyl ketone, i, 162.
 — isopropyl ketone, i, 162.

m-Xylylbutyramide, i, 162.
p-Xylylbutyramide, i, 162.
m-Xylylbutyric acid, i, 162.
p-Xylylbutyric acid, i, 162.
p-Xylylisobutyramide, i, 162.
m-Xylylisobutyric acid, i, 162.
m-Xylylpropylcarbinol, i, 162.

Y.

Yeast, Effront's method for the purification and preservation of, by means of hydrofluoric acid or fluorides, ii, 481.
 Ytterbium group, separation of the metals of the, ii, 283.
 Yttrium chloride, anhydrous, ii, 466.

Z.

Zeolites from Brazil, ii, 422.
 Zinc alkali sulphates, crystallography of, TRANS., 356.
 — ammonium lactate, inactive, TRANS., 1154.
 — — lactates, active, composition and properties of, TRANS., 1151.
 — — — conversion of, into zinc lactates, TRANS., 1153.
 — arsenical, purification of, ii, 209.
 — bromoborate, ii, 519.
 — electrolytic estimation of, ii, 94, 191.
 — electrolytic separation of, from copper, ii, 496.
 — estimation of, ii, 92, 94, 191, 302, 303, 492, 493.
 — ethide, melting point of, ii, 357.
 — — preparation of, i, 196.
 — — spectra of the flame of, ii, 402.
 — fluoride, ii, 321.
 — formation of hydrogen peroxide during the spontaneous oxidation of, ii, 412.
 — glycerates, active and inactive, TRANS., 307.

Zinc, gravimetric estimation of, as sulphide, ii, 302.
 — isopropide, i, 622.
 — manganese, calcium, iron, and aluminium, separation of, ii, 600.
 — methide, melting point of, ii, 357.
 — nitrate, acicular basic, ii, 209.
 — oxide, action of a high temperature on, ii, 168.
 — permanganate, action of heat on, ii, 467.
 — phenylhydrazine sulphate, i, 267.
 — separation of calcium and magnesium from, ii, 344.
 — separation of manganese from, TRANS., 1082.
 — sulphide, phosphorescent, ii, 72.
 — — — as a photometric standard, ii, 202.
 — sulphites, ii, 277, 456.
 — volumetric estimation of, ii, 92, 303, 492.
 — volumetric estimation of, by Schaffner's process, ii, 92.
 — volumetric estimation of, in zinc powder, ii, 492.
 Zinc-antimony-bismuth alloys, ii, 522.
 Zinc-bearing spring waters from Missouri, ii, 81.
 Zinc-bismuth-cadmium alloys, ii, 522.
 Zinc-bismuth-silver alloys, ii, 15.
 Zinc-bismuth-tin alloys, ii, 15.
 Zinc-cadmium-lead alloys, ii, 522.
 Zinc-lead-antimony alloys, ii, 522.
 Zinc-lead-silver alloys, ii, 15.
 Zinc-lead-tin alloys, ii, 15.
 Zincoxides of the alkaline earths, ii, 118.
 Zircon, artificial production of, ii, 128.
 Zirconia, reduction of, by carbon, ii, 532.
 — volatilisation of, ii, 532.
 Zirconiferous felspathic inclusion in basalt, ii, 418.
 Zirconium, extraction of, ii, 532.
 — preparation of, in the electric furnace, ii, 473.
 Zunyite from Colorado, ii, 538.

ERRATA.

VOL. LXII (ABSTR., 1892).

Page	Line	
141	19,	for "there is first formed" read "we may suppose that there is first formed."
784	18*	„ "in 1882" read "in 1882, but these compounds are quite distinct from Recoura's chromosulphuric acid."
1183	11	„ "a crystalline bromo-additive product when treated with bromine water" read "a crystalline additive product with hydrogen bromide."
1228	15	„ "143°" read "145°."
1509	8	„ "proteids" read "albumen."

VOL. LXIV (ABSTR., 1893).

PART I.

17	3*	„ "L. VOLPYAN" read "L. VOLPJAN."
21	2*	„ "A. NEMIROFFSKY" read "A. NEMIROVSKY."
23	13*	<i>et seq.</i> , in the names in italics, for "-idine" read "-idene."
39	15,	for "1 : 4-Amidonaphthalene" read "1 : 4-Ethoxyamidonaphthalene."
52	6*	„ "di- β -naphthyl- α -diketo- $\beta\delta$ -diethylpiperazine" read "di- β -naphthyl- α -diketo- $\beta\delta$ -dimethylpiperazine."
53	15	„ "a-ethoxyisobutyro- β -naphthalide" read "a-ethoxyisobutyro-a-naphthalide."
105	12	„ "and equal" read "although not equal."
127	2	„ "SCHIFFER" read "SCHIFFERER."
168	2*	„ "K. BRUNCK" read "R. BRUNCK."
179	16*	„ "180°" read "280°."
180	6	„ "R. V. ROTTENBURG" read "R. V. ROTHENBURG."
304	17	„ "R. ANSCHÜTZ" read "R. ANSCHÜTZ and W. MONTFORT."
307	15	„ "R. BRAUNSCHWEIG" read "J. W. BRÜHL and R. BRAUNSCHWEIG."
357	5*	„ "Beckmann" read "Elbs (Abstr., 1892, 347)."
379	4	„ "A. SOLDIANI" read "A. SOLDAINI."
387	1	„ "Witt's Oxycellulose. By A. NASTNIKOFF" read "Witt's Oxycellulose." By A. NASTIKOFF."
420	22, 23	„ "S. JUKOFFSKY" read "S. JUKOVSKY."
451	18 <i>et seq.</i> ,	for "ferment" read "enzyme."
451	22*	for "fermenting" read "hydrolytic."
451	9* <i>et seq.</i> ,	for "to ferment" read "to hydrolyse."
451	4*	„ "fermenting" „ "hydrolysing."
506	23*	for "Orthiodosobenzene" read "Orthochloriodosobenzene."
524	21,	for "Zinc" read "Zinc Chloride."
580	15	„ "STAPELBERG" read "E. STAPELBERG."
582	23*	„ "last abstract" read "this vol., i, 580."

VOL. LXIV (ABSTR., 1893).

PART I (cont.).

Page Line

- 615 10, 11, 17, *for* "δ-achroglobulin" *read* "δ-achroglobin."
 618 3*, *for* "V. KISTYAKOFFSKY" *read* "V. KISTYAKOVSKY."
 632 20* "R. T. MAMERT" *read* "R. THOMAS-MAMERT."
 675 18 "W. GÖHLICH" *read* "E. SCHMIDT and W. GÖHLICH."
 713 2* "V. VILLIGER" *read* "A. BAeyer and V. VILLIGER."
 719 16* "Ber., 24" *read* "Ber., 26."
 728 4* " $\text{OH} \cdot \text{C}_9\text{NH}_5\text{Me} < \begin{smallmatrix} \text{CO} \\ | \\ \text{C} \end{smallmatrix}$ " *read* " $\text{OH} \cdot \text{C}_9\text{NH}_5\text{Me} < \begin{smallmatrix} \text{CO} \\ | \\ \text{O} \end{smallmatrix}$ "
 729 12* "Ber., 25" *read* "Ber., 26."
 741 4* "G. VOORHEES" *read* "C. G. VOORHEES."

PART II.

- 9 12* "V. KISTYAKOFFSKY" *read* "V. KISTYAKOVSKY."
 43 7 "Nitrate" *read* "Nitrite."
 107 1 "Electrical into Chemical" *read* "Chemical into Electrical."
 138 23 "algæ" *read* "mosses and algæ."
 " 27 "distinct" *read* "distinct in the *Nostocs*."
 " 28 "similar alga" *read* "alga."
 444 3* "trimethylene" *read* "trimethylethylene."
 453 23* "A. GASSMAN" *read* "A. GASSMANN."
 531 11* "Colombous" *read* "Columbous."
 532 14* *after* "Thorium" *insert* "Oxides."
 533 13* *for* "W. LINDGREN" *read* "W. LINDGREN and W. H. MELVILLE."
 560 1 "C. KELLER" *read* "G. KOTTMAYER."
 601 10* "phenolhydrazol" *read* "phenylhydrazine."

* From bottom.

QD

1

C6

v.64

cop.3

Chemical Society, London
Journal

Physical &
Applied Sci.
Serials

PLEASE DO NOT REMOVE
CARDS OR SLIPS FROM THIS POCKET

UNIVERSITY OF TORONTO LIBRARY

STORAGE

